THE MEASUREMENT OF SILICA ACTIVITIES IN LIQUID SLAGS.

THESIS

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by

JAMES DOUGLAS BAIRD, B.Sc., A.R.T.C.

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ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
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PART I.

THE MEASUREMENT OF SILICA ACTIVITIES IN LIQUID SLAGS BY THE REACTION $SiO_2 + 3C = SiC + 2CO$.

CHAPTER I.

INTRODUCTION.

In the manufacture of iron in the blast furnace one of the most important variables in the composition of the iron produced is the silicon content. Silicon must be kept as low as possible in the manufacture of basic iron in order to reduce the slag bulk in the open hearth furnace. It must also be kept to fairly low limits in making iron for the basic Bessemer process, but in the acid Bessemer process the reverse is true, since here silicon largely determines the heat produced in blowing the iron. Silicon control is also important in the manufacture of foundry iron as it has a major influence on the structure of the cast product.

The main reactions controlling the composition of pig iron in the blast furnace take place in the hearth, where drops of molten iron fall through the slag layer into the bath below, and in so doing react with it. A study of the equilibria between slags and metals of the type obtained in the blast furnace is therefore necessary if the factors controlling pig iron composition are to be fully understood.

Sufficient thermodynamic data are now available for the compounds taking part in these reactions to enable equilibrium constants for the various reactions to be calculated. These equilibrium constants indicate qualitatively the effect which different variables will have on the equilibria, but a quantitative treatment is only possible if the activities of all the reactants in the slag and metal solutions are known.

In the case of some simple systems activities can be estimated or calculated on the basis of thermochemical data, but in the great majority of cases they must be measured experimentally. Usually this is done by bringing the phase being examined into equilibrium with a phase or phases of known thermodynamic properties.

The present work is concerned mainly with the measurement of silica activities in lime-silica and lime-alumina-silica slags. In Part I the method adopted was to measure the carbon monoxide pressure in equilibrium with the slag, silicon carbide and carbon. In Part II the calculation of silica activities from data available on laboratory slag-metal equilibrium measurements has been investigated.

CHAPTER 2.

REVIEW OF PREVIOUS WORK.

The methods employed by previous workers to determine silica activities in molten slags can be divided into four main categories:-

(1) Calculations based on thermodynamic data, phase diagrams and models of the structure of liquid silicates.

(2) Electro-motive force measurements.

(3) Slag-gas equilibria.

(4) Slag-metal equilibria.

These will now be considered in more detail.

(1) Calculations based on Thermodynamic Data, etc.

Activities at some points in binary slag systems can be calculated precisely provided the following data are available:-

(a) the heats of formation of compounds in the system;

(b) the heat capacities of the constituents and their compounds in the solid and liquid states;

(c) the heats and temperatures of fusion.

Unfortunately these data are known accurately for a very few systems only, but this method has been used by Darken(1) and by Richardson(2) for the $CaO-SiO_2$ system, for which some of the above data were available.

The other methods of calculation which follow are of either an empirical or semi-empirical nature.

Early examination of slag systems was concerned mainly with the determination of phase diagrams. In trying to apply the data thus acquired to reactions involving liquid slags, compounds stable in the solid slag were postulated to exist also in the liquid slag. By correct choice of compounds and in some cases by the assumption of some degree of dissociation of these compounds in the liquid state, an attempt was made to estimate the amount or concentration of a constituent which would be "free" to take part in a chemical reaction. This quantity bears some relation to the more exact thermodynamic function of the activity of the component.

The compound approach to the study of liquid slags can only be empirical and approximate due to the differences in structure between solid and liquid slags, and the difficulty of knowing how compound dissociation is affected by other constituents and by temperature. Nevertheless its use has given results of considerable practical importance, as in the early work of Schenck(3) in estimating "free" concentrations of reactants in steelmaking slags, and in the interpretation of the sulphur equilibrium between metal and slag in terms of "excess base" by Grant and Chipman(4). This method is now mainly useful in dealing with the complex slags used in practice, and is likely to be replaced by more exact thermodynamic methods as these are extended.

In calculating "free" concentrations of reactants, Schenck assumed that the compounds present in the solid state were partially dissociated in the liquid state. This concept was also used by White(5) in interpreting oxygen pressure measurements on iron oxide slags containing lime and silica. Subsequently Murray and White(6) deduced the

activities of lime and silica in $CaO-SiO_2$ melts from dissociation constants for the compounds $CaO.SiO_2$ and $2CaO.SiO_2$ obtained from White's previous work. Although this is not an exact thermodynamic treatment, it does appear to predict fairly accurately the interaction of lime and silica in the liquid state.

Rey(7) calculated the activity of silica in a number of binary metal oxide-silica systems (including the $CaO-SiO_2$ system), making use of the shape of the silica saturation curve (or lowering of the freezing point) at high silica activities and assuming the solution to be "regular". The concept of the "regular solution" was introduced by Hildebrand(8), and implies that the mixing of molecules or ions is completely random. However, accurate data compiled by Richardson(2) or the $CaO-B_2O_3$ system suggests that the assumption of regularity for melts of this type may lead to considerable errors in the calculation of activities.

Ideally it would be desirable to be able to calculate activities of constituents in liquid slags on the basis of some model of the structure of the liquid. Conductivity and electro-motive force measurements have revealed that liquid slags contain ions, and various attempts have been made to calculate activities using some ionic model of slag structure.

Herasymenko(9) and Herasymenko and Speight(10) assumed the complete ionisation of liquid slags and made use of the mass action equation by replacing activities by ionic fractions. The ionic

fraction of a constituent ion was taken as the ratio of the number of gm-ions of that type to the total number of gm-ions present. This assumption would seem to be an over-simplification, as it implies that ions of different signs mix randomly, whereas a state of lower free energy would be reached if ions of opposite charge associated preferentially with each other. In consequence this treatment cannot be used satisfactorily for a wide variety of slag-metal reactions.

Temkin(11) also assumed the complete ionisation of liquid slags, but he expressed ionic concentrations as fractions of the number of gm-ions of the same sign. This allows for the preferential association of cations and anions, but assumes that this association is random.

Flood, Førland and Grjotheim(12) have attempted to take into account differences in interaction energies between different ionic species in the melt, while still assuming that the cations (and similarly the anions) are randomly distributed with respect to themselves. This method has been successfully employed in interpreting a number of equilibria involving basic slags. However, it requires a knowledge of the ionic species present in the melt, and so its application to more highly siliceous slags, where the state of association of silica is not definitely known, is likely to prove more difficult.

(2) Electro-Motive Force Measurements.

In order to measure the activity of silica in a liquid melt by this method it is necessary to set up a reversible cell in which a known reaction, involving the silica dissolved in the slag, takes place.

Chang and Derge(13) used electrodes of silicon carbide and graphite (the latter forming the crucible) to construct a cell of this type. The cell reaction was not known, and had to be inferred from an examination of the E.M.F. values obtained. The results obtained in the lime-silica binary appear feasible, but the iso-activity curves in the $CaO-SiO_2-Al_2O_3$ do not slope in the direction expected from the position of the silica saturation curve (which is the iso-activity curve for $a_{SiO_2} = 1$).

(3) Slag-Gas Equilibria.

The use of slag-gas equilibria for the measurement of slag activities is attractive because of the thermodynamic simplicity of the gas phase. Due to this advantage the results are more easily interpreted than are data on equilibria with complex metallic solutions.

Unfortunately it is difficult to apply this technique directly to the determination of silica activities due to the difficulty of devising suitable reactions. It is possible to overcome this difficulty in the case of some binary silicate melts by determining the activity of the second component and using the Gibbs-Duhem relation to determine the activity of silica.

The activity of FeO in slags can be determined by bringing the slags into equilibrium with gas mixtures of controlled oxygen pressure while the slags are held in a crucible with a known iron activity. This method has been successfully applied to $FeO-SiO_2$ slags by Schuhmann and Ensio(14), and to more complex slags by Michel and Schuhmann(15) and Taylor and Chipman(16), and some of these results may be used to deduce

silica activities in high-FeO slags.

Results of more direct interest to the present work have been obtained from determinations of lime activities. In recent studies by Fincham and Richardson(17) and Carter and Macfarlane(18) the slag-gas technique has been used to determine the sulphur capacity of slags. The equilibrium established can be expressed by the equation :

$$(CaO) + \tfrac{1}{2}S_2 = (CaS) + \tfrac{1}{2}O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

(round brackets indicate solution in the slag phase).

The activity coefficient of calcium sulphide was not known over the wide range of compositions examined, but if it is assumed to be constant at concentrations well below saturation, the results obtained can be used to calculate lime-activities in lime-silica slags. Silica activities may then be obtained by the Gibbs-Duhem relation. Results obtained(19) in the $CaO-Al_2O_3-SiO_2$ system can also yield approximate values of a_{SiO_2} in these slags by means of the Gibbs-Duhem relation if the activity of alumina is assumed to be constant along lines of constant $N_{Al_2O_3}$.

(4) Slag-Metal Equilibria.

Chipman and co-workers(20)(21) have determined experimentally the silicon contents of carbon-saturated iron in equilibrium with $CaO-Al_2O_3-SiO_2$ slags at temperatures from 1425-1700°C according to the reaction

$$(SiO_2) + 2C = \underline{Si} + 2CO \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

(underlining indicates solution in the metal phase).

The carbon monoxide pressure under which the experiments were carried out was 1 atmosphere. The slow reaction rate was increased by the use of a graphite stirrer, but despite this the equilibrium compositions could not be established with great accuracy at the lower temperatures.

From these results, silica activities in the slag can be calculated providing only that the silicon activity in the metal is known. In the second of the two papers, Fulton and Chipman carried out this calculation using the data of Chipman, Fulton, Cokcen and Caskie(22) on the activity of silicon in Fe-Si-C alloys. These data were obtained by measurements of silicon distribution between immiscible Fe-Si-C and Ag-Si liquids. Extrapolation of these data (especially at the low-silicon high-carbon end) was necessary to cover all the compositions required for slag activity calculations, but recent studies of silicon activities in this range of compositions by Arthur(23) indicated that the extrapolated values of a_{Si} used by Fulton and Chipman in this range were likely to be low.

Sanbongi and Ohtani(24) have combined the slag-metal and slag-gas techniques by studying the reduction of silica in a slag by hydrogen in the presence of iron, according to the reaction:-

$$(SiO_2) + 2H_2 = \underline{Si} + 2H_2O \qquad \text{.....(3)}$$

By using a lime crucible theequilibrium was established for the case of a $CaO-SiO_2$ slag saturated with Ca_2SiO_4. In the calculation of silica

activity in this slag Sanbongi and Ohtani used their own values for a_{Si} in Fe-Si alloys, which were derived in a similar way but using a pure silica crucible. They found that the activity of silicon obeyed Henry's Law up to 10 per cent silicon, a finding which is contrary to that of Chipman, Fulton, Gokcen and Caskie(22).

Summary.

Although a considerable amount of work has been done on the activity of silica in the lime-silica system, the results obtained are open to some doubt due to the assumptions which have had to be made in most cases. More accurate data is thus necessary, especially at the more basic compositions. In the more complex systems obtained in practice, the approximate effects of the addition of other oxides are known but accurate data suitable for calculations is not yet available.

Equilibrium of Slags with Silicon Carbide.

In the course of their slag-metal studies, Chipman and co-workers (20),(21), noted the fact that at high silica contents silicon carbide became stable, co-existing with the slag and metal according to the equilibria.

$$(SiO_2) + 3C = SiC + 2CO \quad \text{.....(4)}$$

$$(SiO_2) + 2C = \underline{Si} + 2CO \quad \text{.....(3)}$$

$$\underline{Si} + C = SiC \quad \text{.....(5)}$$

The actual slag composition in equilibrium with silicon carbide, carbon and 1 atmosphere pressure of carbon monoxide was determined

experimentally in only one series of runs at 1600°C. At other temperatures the silicon carbide saturation point was obtained from previous determinations(22) of the equilibrium silicon content for reaction (5). Slag in equilibrium with this metal composition must also be saturated with silicon carbide.

As far as the writer knows, no work has been done on the equilibrium conditions for reaction (4) at pressures other than 1 atmosphere.

CHAPTER 3.

THE Si-C-O SYSTEM.

(a) Theoretical.

(1) Free Energy Data.

In the present work it was considered that silica activities in liquid slags could be determined accurately by measuring the carbon monoxide pressure of the reactions:-

$$(SiO_2)_{slag} + 3C = SiC + 2CO \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

If this were the only reaction possible between the slag, carbon, and silicon carbide, it would be possible to measure the reaction pressure by holding these three reactants in a graphite or silicon carbide crucible, and heating this crucible inside a pressure-tight reaction vessel connected to a manometer.

This simple system is, however, complicated by the fact that gaseous silicon monoxide can be produced in it by the two reactions:-

$$(SiO_2)_{slag} + C = SiO(g) + CO \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$SiC + CO = SiO(g) + 2C \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

If the reactants were held in an open crucible, silicon monoxide gas would be able to diffuse rapidly away from the reaction zone and condense on the cooler parts of the reaction vessel. The silicon monoxide pressure above the reactnats would thus always be lower than that in equilibrium at the prevailing carbon monoxide pressure according to reactions (2) and (3). Reactions(2) and (3) would therefore proceed from left to right in order to restore equilibrium, and carbon monoxide would be evolved and absorbed at rates depending on the relative reaction rates of (2) and (3). The effect of the diffusion and condensation of gaseous silicon monoxide must thus be to set up a dynamic equilibrium.

True equilibrium can only be attained in this system if the reaction vessel is enclosed and at a temperature above that at which silicon monoxide gas can condense. It is not experimentally possible to measure the pressure in such a system, and the method used in this work was to hold the reactants in a small cylindrical graphite crucible whose mouth was closed by a graphite plug. This plug contained a small capillary hole, which was large enough to allow equalisation of the total pressures inside and outside the crucible, but small enough to reduce silicon monoxide diffusion to a level sufficiently low to prevent the silicon monoxide pressure falling appreciably below that in equilibrium in the static system.

Since the thermodynamic data on the reactants in equation(1) appeared to be well established, it was considered when the work was begun that the activity of silica in a slag could be obtained directly from the value of K_1 $(= p_{CO}^2/a_{SiO_2})$ as calculated from these data, when the value of p_{CO} had been measured.

Using the method outlined above reaction pressures were determined for a series of $CaO-SiO_2$ slags of compositions extending up to silica saturation in the temperature range 1450-1550°C. The results obtained were not completely consistent, but they indicated that the reaction pressures were much lower than would be predicted from the available thermodynamic data for reaction(1). For example, the values of p_{CO} for a silica saturated slag at 1500°C were in the range of 0.7 - 0.9 atmospheres, compared with the calculated values of 1.50 atm. It was

therefore considered necessary to carry out a full theoretical study of the simple Si-C-O system, with special reference to the experimental conditions used in the slag experiments, under which diffusion of gaseous silicon monoxide away from the reaction zone is restricted. The Si-C-O system was also studied experimentally before experiments with slags were resumed.

In studying the reactions from a theoretical viewpoint a knowledge of the possible compounds which may be stable is necessary. Under the extremely reducing experimental conditions the only gases in the Si-C-O system which are likely to be present in appreciable quantities are carbon monoxide and silicon monoxide. The only solid compounds definitely known to be stable are silica and silicon carbide, but in addition various workers claim to have established the existence of crystalline silicon monoxide, stable only at high temperatures, and of various silicon-carbon-oxygen compounds such as siloxicon (Si_2C_2O).

From the thermodynamic data available for the compounds known to be stable, reaction pressures can be calculated under various conditions. As it will be necessary to compare the experimental results with those obtained by calculation, the thermodynamic data available for the compounds silica, silicon carbide, carbon monoxide and gaseous silicon monoxide will now be reviewed. For calculation purposes the most convenient thermodynamic function for these compounds is their free energy of formation. Since this free energy can be expressed to the required degree of precision by an equation of the form-

$$\Delta G^\circ = x + y.T$$

(where T is the temperature in °K), the result of other workers will all be expressed in this form.

Silica.

Humphrey, Todd, Coughlin and King(25) have calculated the free energies of formation of quartz and liquid silica form the heat of formation, as determined by Humphrey and King(26) and from entropy data compiled by Kelley(27). Their tabulated results lead to the following equations for the free energy of formation of "high" (β) quartz:-

$$Si(c) + O_2 = SiO_2 \ (\beta \text{ quartz})$$

$$\Delta G^\circ = -207{,}700 + 40{\cdot}7\ T \quad (848°K - 1683°K)$$

The heat of fusion of silicon was determined by Körber and Olsen(28) to be 11,100 cal./gm.mole, so that, as silicon melts at 1683°K, the free energy of fusion $\Delta G^\circ = 11{,}100 - 6.59\ T$.

It follows that for:-

$$Si(l) + O_2 = SiO_2 \ (\beta \text{ quartz})$$

$$\Delta G^\circ = -218{,}800 + 47.3\ T \quad (1683°K - 1883°K).$$

The free energy of formation of β cristobalite from liquid silicon and oxygen has been calculated by Gokcen and Chipman(29), again using the data of Humphrey and King(26) and Kelley(27), giving for the system:-

$$Si(l) + O_2 = SiO_2 \ (\beta \text{ cristobalite})$$

$$\Delta G^\circ = -217{,}700 + 47.0\ T \quad (1683\text{-}2000^\circ K)$$

From the free energy of fusion of silicon given above:-

$$Si(C) + O_2 = SiO_2 \ (\beta \text{ cristobalite})$$

$$\Delta G^\circ = -206{,}600 + 40.4\ T.$$

Examination of these equations shows that up to 3,700°K the calculated free energy of formation for β quartz is always more negative than that calculated for β cristobalite. Since cristobalite is the most stable form of silica above 1470°C, the equations must be in error. Both calculations have been checked and found to be correct, so that the error must lie in the experimental data on which they are based. The heat of transformation, α quartz $\rightarrow \alpha$ cristobalite, was found to be +930 cal. at 298°K by Humphrey and King(26), and this value must be about 400 cal. too high, or else the heat content data should indicate a larger difference in entropy between quartz and cristobalite.

Due to the inability of the present data to differentiate satisfactorily between the different forms of silica, the equation for β quartz has been used in subsequent calculations for all forms of silica. Being the more negative of the two, it should be closer to the true β cristobalite equation than is the calculated β cristobalite line.

Silicon Carbide.

Humphrey, Todd, Coughlin and King(25) have determined $\Delta H^{\circ}_{298^{\circ}K}$ for both cubic and hexagonal silicon carbide by combustion in oxygen. The silicon carbide was mixed with titanium powder prior to ignition in order to ensure complete combustion. They have also determined the high and low temperature heat capacities for both varieties. The heats of formation obtained were:-

Si + C = SiC (Hex.modification II): $\Delta H_{298.16}$ = -12,310+920 cal.per mole.

Si + C = SiC (cubic) : $\Delta H_{298.16}$ = -13,400±920 cal.per mole.

These values are considerably lower than those reported by previous workers. The low temperature heat capacities showed excellent agreement with the values obtained by Kelley(30) for the hexagonal modification, and the high temperature heat capacities are also in good agreement with previous determinations(27).

Humphrey et.al(25) have calculated the free energy of formation of silicon carbide from their experimental data. There is a small difference between the values obtained for the cubic and hexagonal modification, but for general purposes a mean value may be taken, viz.,

Si(C) + C = SiC : ΔG° = -13,300 + 1.71 T. (900-1683°K)

Si(I) + C = SiC : ΔG° = -24,400 + 8.3 T (1683-2000°K)

The free energy of formation of silicon carbide obtained in this way from thermochemical data agrees very well with measurements made by Chipman, Fulton, Gokcen and Caskey(22) of the activity of silicon in Fe-Si-C alloys saturated with graphite and silicon carbide. The data of Humphrey et al(25), therefore seemed to be well established when the present work was begun.

Carbon Monoxide.

The free energy of formation of carbon monoxide is now established accurately by a number of workers. The National Bureau of Standards "Selected Values of Thermodunamic Properties" recommends the equation:-

$$C + \tfrac{1}{2}O_2 = CO \; ; \; \Delta G^\circ = -28{,}100 - 20.2\,T$$

Silicon Monoxide.

The existence of gaseous silicon monoxide has now been firmly established spectroscopically. Since it is formed from silica at high temperatures under reducing conditions, it is bound to be present under the experimental conditions existing in the present work.

The possibility of interference in the measurement of the carbon monoxide pressure of the reaction:-

$$SiO_2 + 3C = SiC + 2CO \qquad \ldots\ldots\ldots\ldots (4)$$

due to diffusion of silicon monoxide has already been outlined, and will be dealt with in greater detail at a later stage. In addition to this effect, the presence of gaseous silicon monoxide must increase the measured reaction pressure from p_{CO} to $p_{CO} + p_{SiO}$, and hence a knowledge of the thermodynamic data for silicon monoxide gas is necessary in order to obtain the values of the carbon monoxide pressures from the measured reaction pressures. A knowledge of the thermodynamic properties of solid silicon monoxide is also desirable, since if solid silicon monoxide were stable under the experimental conditions, the presence of a fourth solid phase in the Si-C-O system would render either silica or silicon carbide unstable and lead to a different equilibrium from that expressed by equation (4).

Gaseous silicon monoxide is most commonly produced by the reduction of silica either by carbon or by silicon at temperatures over about 1200°C. The vapour may be condensed on a chilled surface to form a black vitreous substance which has been shown by X-ray analysis and electron diffraction to be practically amorphous, with only a limited amount of short range order. If the condensation of the vapour is less rapid a mixture of very finely divided silica and silicon is formed. The amorphous substance produced by rapid chilling of the vapour, quickly breaks down to a mixture of silicon and silica when annealed in the range of 400-1000°C (approximately) Solid silicon monoxide is thus thermodynamically unstable with respect to silicon and silica at these temperatures.

There is some evidence, however, that crystalline silicon monoxide does become stable at higher temperatures. The most convincing support for the high temperature stability of solid silicon monoxide was obtained by Brewer and Edwards(31) by means of a "thermoelectric valve". This was based on the observations of Gel'd and Kochnev(32) and Erasmus and Persson(33) that solid SiO has a very high electrical resistance. A heating element consisting of an equimolecular mixture of silicon and silica in a quartz glass tube was heated by applying a fixed voltage across the ends. At a certain point the resistance of the rod rose sharply and a bright boundary layer was formed which extended across the narrowest cross-section of the rod. The temperature of the boundary was found to be 1461 ± 22°K. The bright boundary layer was interpreted as the point at which solid SiO was being formed due to increase in temperature, and then disproportionating again due to the drop in

current consequent on the increase in resistance of the rod.

In addition to this, Potter(34) and Brewer and Edwards(31) have both tried to melt equimolecular mixtures of silicon and vitreous silica, and have found that the softening point is above 1700°C - higher than would be expected for the mixture.

Despite this physical evidence for its formation, solid silicon monoxide has not yet been definitely identified structurally. Brewer and Edwards(31) attempted to obtain it by quenching an Si + SiO_2 mixture from 1300° but found no evidence of its presence. This has been confirmed by experiments carried out in conjunction with the present work(35). A mixture of mole ratio $Si/SiO_2 = 1/3$ showed no diminution in intensity of silicon X-ray lines after quenching from 1350°C, and no evidence of a decrease in particle size was observed. Such a decrease might be expected if the silicon had been produced by the solid reaction:-

$$2SiO(solid) = Si + SiO_2 \qquad \text{.....(5)}$$

Hoch and Johnstone(36) claimed to have detected crystalline silicon monoxide by high temperature X-ray camera. However, Geller and Thurmond (37) have suggested that the new lines obtained by Hoch and Johnstone were due to β -cristobalite and β silicon carbide.

The question of the existence of solid silicon monoxide is of importance in establishing the thermodynamic properties of gaseous SiO from the experimental data available. Several determinations have been made (32),(38),(39), of the SiO pressures above mixtures of silicon and silica. If the results of Brewer and Edwards' thermoelectric valve experiments are accepted, then the values of p_{SiO} obtained above 1460°K

should refer to the vapour pressure of solid SiO, while those measured below this temperature should refer to the reaction:-

$$Si + SiO_2 = 2SiO(g) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

The most accurate measurements of p_{SiO} for this latter reaction appear to be those of Schafer and Hornle(38). As shown by Humphrey et al(25) their results in the temperature range 1336-1429°K give very consistent values of $\Delta H^\circ_{298.16}$ for reaction (6). Brewer and Edwards(31) consider that the larger apparent error in $\Delta H^\circ_{298.16}$ obtained from their measurement at 1460°K is due to the stability of solid SiO at this temperature.

The free energy of formation of gaseous silicon monoxide has been calculated from heat of formation data derived from Schäfer and Hörnle's results, and from entropy values derived from spectroscopic data given by Herzberg(40) and the tabulated data of Kelley(27). The following equations were obtained:-

$$Si(C) + \tfrac{1}{2}O_2 = SiO(g) \; ; \; \Delta G^\circ = -25{,}100 - 17.97\,T \quad (1200\text{-}1683^\circ K)$$

$$Si(l) + \tfrac{1}{2}O_2 = SiO(g) \; ; \; \Delta G^\circ = -36{,}340 - 11.30\,T. \quad (> 1683^\circ K)$$

These equations agree well with the values calculated in a similar way by Humphrey, Todd, Coughlin and King(25).

Brewer and Edwards(31) have reviewed the other experimental studies from which $\Delta H^\circ_{298.16}$ for the formation of gaseous silicon monoxide can be obtained. Confirmation of the value obtained from Schäfer and Hörnle's measurement is obtained from the work of Brewer and Mastick (41) on the reaction $SiO_2 = SiO(g) + \tfrac{1}{2}O_2$, and from some of Tombs and Welch's(39) data on the

reaction $SiO_2 + H_2 = SiO(g) + H_2O$. Gel'd and Kochnev's(32) measurements of p_{SiO} over silicon and silica yield a rather lower value of $\Delta H^\circ_{298.16}$ as do Grube and Speidel's investigations of the reaction $SiO_2 + H_2 = SiO(g) + H_2O$.

Brewer and Edwards(31) have also attempted to calculate the free energy of formation of solid silicon monoxide. Using mainly data on the amorphous solid they conclude that ΔG° for the reaction

$$Si + SiO_2 = 2SiO(s) \quad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

is likely to become slightly negative at high temperatures. Due to the low accuracy of the data on which the calculation is based, this conclusion is only tentative.

(2) Reaction Pressures.

The above thermodynamic data will now be used to calculate the equilibrium reaction pressures in the Si-C-O system.

(a) The Reaction $SiO_2 + 3C = SiC + 2CO$ .....(4)

By combining the free energies of formation of the reactants, ΔG°_4* for this reaction amy be obtained, viz.,

$$\Delta G^\circ_4 = 137{,}900 - 79.4\ T$$

Since $-\Delta G^\circ_4 = R\ T \log_e K_4$

$$\log_{10} K_4 = 17.35 - \frac{30{,}140}{T}$$

* ΔG°_x and K_x refer to the standard free energy change and equilibrium constant for the reaction numbered (x) in the text.

where the solid reactants are present in their standard states

$K_4 = p_{CO}^2$, the carbon monoxide pressure of the reaction can be calculated for different temperatures. The values obtained in the range 1300-1600°C are shown in Table I.

TABLE I.

Calculated values of p_{CO} in equilibrium with SiO_2, SiC and C.

T°C	p_{CO}(atm.)	T°C	p_{CO}(atm.)
1300	0.124	1500	1.503
1350	0.246	1550	2.564
1400	0.466	1600	4.256
1450	0.849		

(b) The Reaction $SiO_2 + C = SiO(g) + CO$ .....(7)

The equilibrium constant for this reaction can be calculated by a similar process to give:-

$$\Delta G^\circ_7 = 154,360 - 78.8\ T$$

$$\log K_7 = 17.22 - \frac{33,750}{T}$$

where $K_7 = p_{SiO} \times p_{CO}$

The calculated value of K_7 from 1300-1600°C are shown in Table II.

TABLE II.

Calculated values of $p_{SiO} \times p_{CO}$ in equilibrium with SiO_2 and C.

T°C	$K_7(p_{SiO} \times p_{CO})$	T°C	$K_7(p_{SiO} \times p_{CO})$
1300	5.90×10^{-5}	1500	1.55×10^{-2}
1350	2.63×10^{-4}	1550	5.12×10^{-2}
1400	1.12×10^{-3}	1600	1.62×10^{-1}
1450	4.26×10^{-3}		

By substituting the values of p_{CO} given in Table I, the value of p_{SiO} in equilibrium with SiO_2, SiC and C may be calculated. The values obtained are shown in Table III.

TABLE III.

Calculated values of p_{SiO} in equilibrium with SiO_2, SiC and C.

T°C	p_{SiO}(atm).	T°C	p_{SiO}(atm).
1300	4.76×10^{-4}	1500	1.03×10^{-2}
1350	1.07×10^{-3}	1550	2.00×10^{-2}
1400	2.40×10^{-3}	1600	3.81×10^{-2}
1450	5.02×10^{-3}		

If complete equilibrium is established in the system SiO_2, SiC C, gas, the total gas pressure should be equal to $p_{CO} + p_{SiO}$.

(3) Effect of Silicon Monoxide Diffusion on the Reaction Pressures.

(a) Silica and Carbon.

In the absence of silicon carbide the carbon monoxide pressure of this system should be controlled by the value of p_{SiO} in the system, the product $p_{SiO} \times p_{CO}$ being given in Table II. If the reaction system is not completely enclosed the silicon monoxide will tend to diffuse out of the system, and as p_{SiO} falls, p_{CO} will rise correspondingly. The rate at which the pressure rises will depend on the rate at which p_{SiO} can fall by diffusion.

At values of p_{CO} below the equilibrium values for the reaction:-

$$SiO_2 + 3C = SiC + 2CO \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

some of the silicon monoxide formed by reaction (7) may be consumed by the reaction:-

$$SiO(g) + 2C = SiC + CO \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3')$$

Thus, in this range of pressures, gaseous silicon monoxide may act as an intermediate step in the production of silicon carbide. At values of p_{CO} above that for reaction (4), silicon carbide is unstable, and gaseous silicon monoxide should be the only reduction product of silica (assuming for the present that no other intermediate compounds exist).

(b) Silicon Carbide.

Similar conclusions are obtained when silicon carbide is present alone. At carbon monoxide pressures above those for reaction (4), the net reaction is:-

$$SiC + 2CO = SiO_2 + 3C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4')$$

which may take place in the two steps:-

$$SiC + CO = SiO(g) + 2C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3')$$

$$SiO(g) + CO = SiO_2 + C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7')$$

In addition some gaseous silicon monoxide must escape from the reaction zone by diffusion before conversion to silica and carbon.

At lower carbon monoxide pressures silica is unstable and gaseous silicon monoxide should be the only product of the reaction between silicon carbide and carbon monoxide. If this gaseous silicon monoxide can escape from the reaction zone and condense in a colder part of the system, the ratio $p_{SiO}/p_{CO} = K_8$ can only be maintained constant by the absorption of more carbon monoxide in the production of gaseous silicon monoxide. The net effect should thus be a gradual fall in the value of $p_{CO} + p_{SiO}$ until $p_{CO} = p_{SiO}$.

(c) Silica, Silicon Carbide and Carbon.

As shown in paragraphs (a) and (b), if silica and carbon only are present the value of p_{CO} may drift above that for reaction (4), while if silicon carbide alone is present it may drift slowly below it.

In the case where all three are present together, it must be assumed that diffusion of gaseous silicon monoxide to the colder areas

of the system will reduce the value of p_{SiO} to slightly below that in equilibrium with the three solids. In an attempt to reach the equilibrium value of p_{SiO} two reactions will take place, viz.,

$$SiO_2 + C = SiO(g) + CO \quad \text{.....(7)}$$

$$\text{and } SiC + CO = SiO(g) + 2C \quad \text{.....(3).}$$

If the original carbon monoxide pressure was that in equilibrium according to the reaction

$$SiO_2 + 3C = SiC + 2CO \quad \text{.....(4)}$$

and if reactions (7) and (3) took place at equal rates, then the value of p_{CO} would remain constant no matter how much p_{SiO} fell below the equilibrium value due to diffusion, since carbon monoxide would be evolved and absorbed in equal amounts in an attempt to restore the silicon monoxide equilibrium.

A wide difference between the reaction rates of (7) and (3) would cause some deviation from the equilibrium value of p_{CO} for reaction (4). This effect should be slight, however, since p_{SiO} is very small (as is shown in Table III). In consequence only a small amount of reaction is possible, and the amounts of carbon monoxide being evolved by reaction (7) and absorbed by reaction (3) must be small. In the experimental measurement of the reaction pressures of reaction (4), any error due to this effect can be reduced or eliminated by reducing the diffusion of silicon monoxide from the reaction zone, and by increasing the reaction rates of (7) and (3) (for example by improving contact between the particles).

In the present experiments diffusion has been cut down by carrying out the reactions in a graphite crucible completely enclosed except for a fine capillary. The reaction pressures observed should thus approach the equilibrium values of $p_{CO} + p_{SiO}$ very closely. If no other solid phases are stable under the experimental conditions, the simple pressure/temperature/composition diagram shown in Fig.1 should be obtained.

4. Effect of Existence of Another Solid Compound.

The possible existence of some solid compound other than SiO_2 and SiC in the Si-C-O system was noted earlier. No structural or thermodynamic data is available for any such compound, but it is possible that some compound which breaks down on cooling to a mixture containing silica, silicon carbide and carbon may have remained undetected by X-ray examination.

As was shown previously, the thermodynamic data available for silicon monoxide indicates that ΔG° for the reaction:-

$$Si + SiO_2 = 2SiO(s) \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

may become slightly negative at high temperatures. If this is the case the vapour pressure of solid silicon monoxide should be slightly less than the silicon monoxide pressure for the reaction

$$Si + SiO_2 = 2SiO(g) \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

since the stable configuration should have the lower vapour pressure. Calculated values of p_{SiO} for reaction (6) are shown in Table IV.

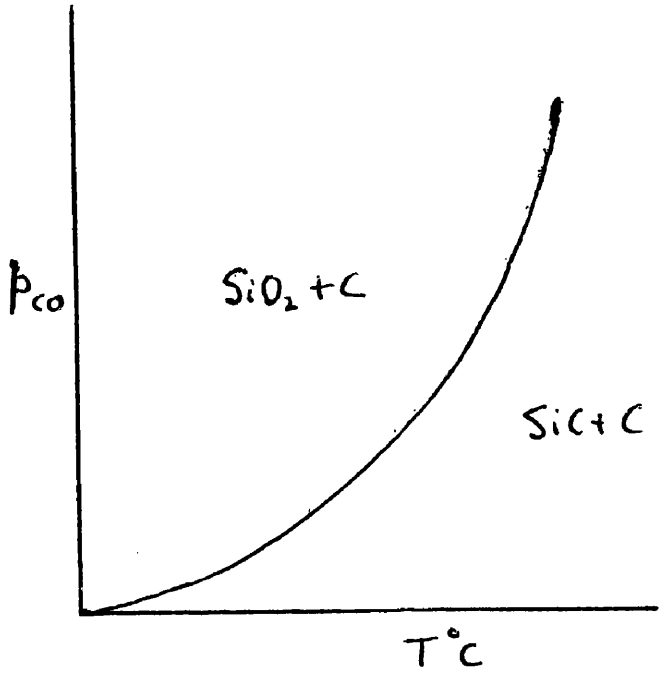


Fig.1.

Simple pressure/temperature diagram for Si-C-O system if SiO_2 and SiC are the only stable solid compounds.

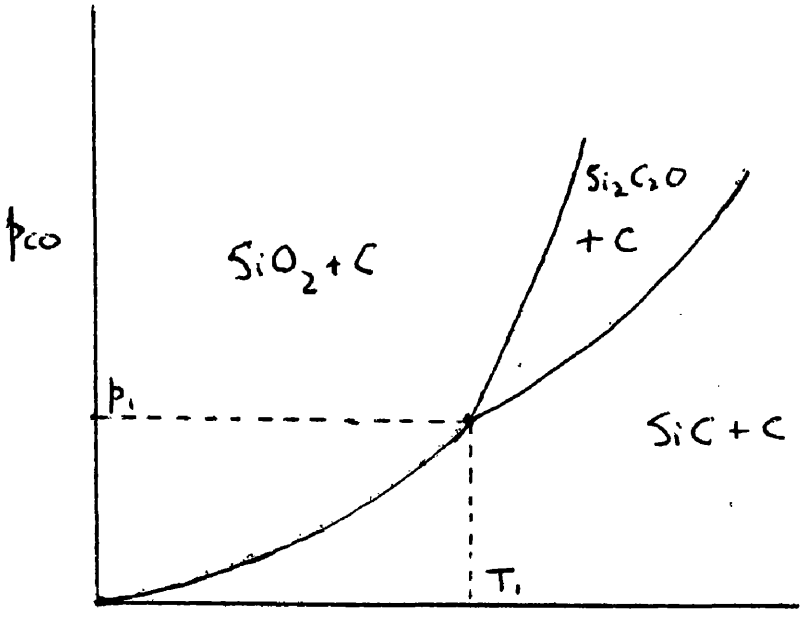


Fig.2.

Type of pressure/temperature diagram proposed by Brunner(43).

TABLE IV.

Calculated values of p_{SiO} in equilibrium with SiO_2 and Si.

T°C	p_{SiO}(atm.)
1400	1.14×10^{-3}
1450	2.88×10^{-3}
1500	4.68×10^{-3}
1550	8.13×10^{-3}
1600	1.38×10^{-4}

As can be seen by comparison with Table III these pressures are some three to four times higher than the silicon monoxide pressures calculated to be in equilibrium with silica, carbon, and silicon carbide. Thus, due to the comparatively higher stability of silicon carbide, solid silicon monoxide is unlikely to be stable in the presence of carbon.

Brunner(43) has investigated reaction pressures in the Si-C-O system. The results obtained will be discussed quantitatively later.

The type of diagram proposed to explain the results is shown in Fig.2. A compound siloxicon (Si_2C_2O) was said to be stable at temperatures above T_1 (1560°C). The existence of another solid phase reduces the number of degrees of freedom from one to none, that is, the 4 solid phases can coexist at only one temperature and pressure T_1 and p_1). Above T_1 a mixture of silica, silicon carbide and carbon becomes unstable and,

in the presence of excess carbon, either silica or silicon carbide must disappear. By suitable variation of the initial composition of the mixture it should be possible to obtain the reaction pressures for the two reactions:

$$2SiO_2 + 5C = Si_2C_2O + 3CO \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$\text{and } Si_2C_2O + C = 2SiC + CO \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

A similar type of diagram would be obtained if solid silicon monoxide were formed at high temperatures, or if any ternary compound other than siloxicon existed which broke down on cooling.

The presence of any such compound should be detectable by the measurement of reaction pressures. If the breakdown temperature lies within the temperature range examined, a break in p_{CO}/T curve should be obtained. It should also be possible to measure two distinct reaction pressures above the breakdown temperature by varying the composition of the reaction mixture.

CHAPTER 4.

THE Si-C-O SYSTEM.

(b) Experimental.

Experimental Measurement of Reaction Pressures in the Si-C-O System.

(1) Apparatus.

The main requirement for the accurate measurement of reaction pressures of the slow reactions in this system is to construct a reaction vessel of small volume which will remain leak proof over long periods at the high experimental temperatures. The apparatus used in the present work consisted in the main of a horizontal platinum-wound resistance furnace, with an inner furnace tube of mullite or recrystallised alumina. The use of a horizontal furnace eliminated fluctuations in the measured pressure due to convection currents. A diagram of the apparatus is shown in Fig.3.

The platinum-13% rhodium wound furnace operated satisfactorily, although considerable loss of platinum by volatilisation was inevitable over the very long periods of use. The winding tube was made from alundum cement, and the winding was surrounded by shaped bricks made from alundum which had been rendered porous by the addition of sawdust to the mix before firing. These bricks prevented contamination from the less refractory insulating bricks, cut down heat loss from convection and made dismantling of the furnace much easier than is the case if powdered alumina is used.

In the first 20-30 runs attempted, great difficulty was experienced due to the failure of furnace tubes and thermocouple sheaths. This difficulty was accentuated by the presence in the tubes after use of surface-active deposits which rendered the complete evacuation of such tubes a very lengthy job. In consequence it was impossible in some cases to establish

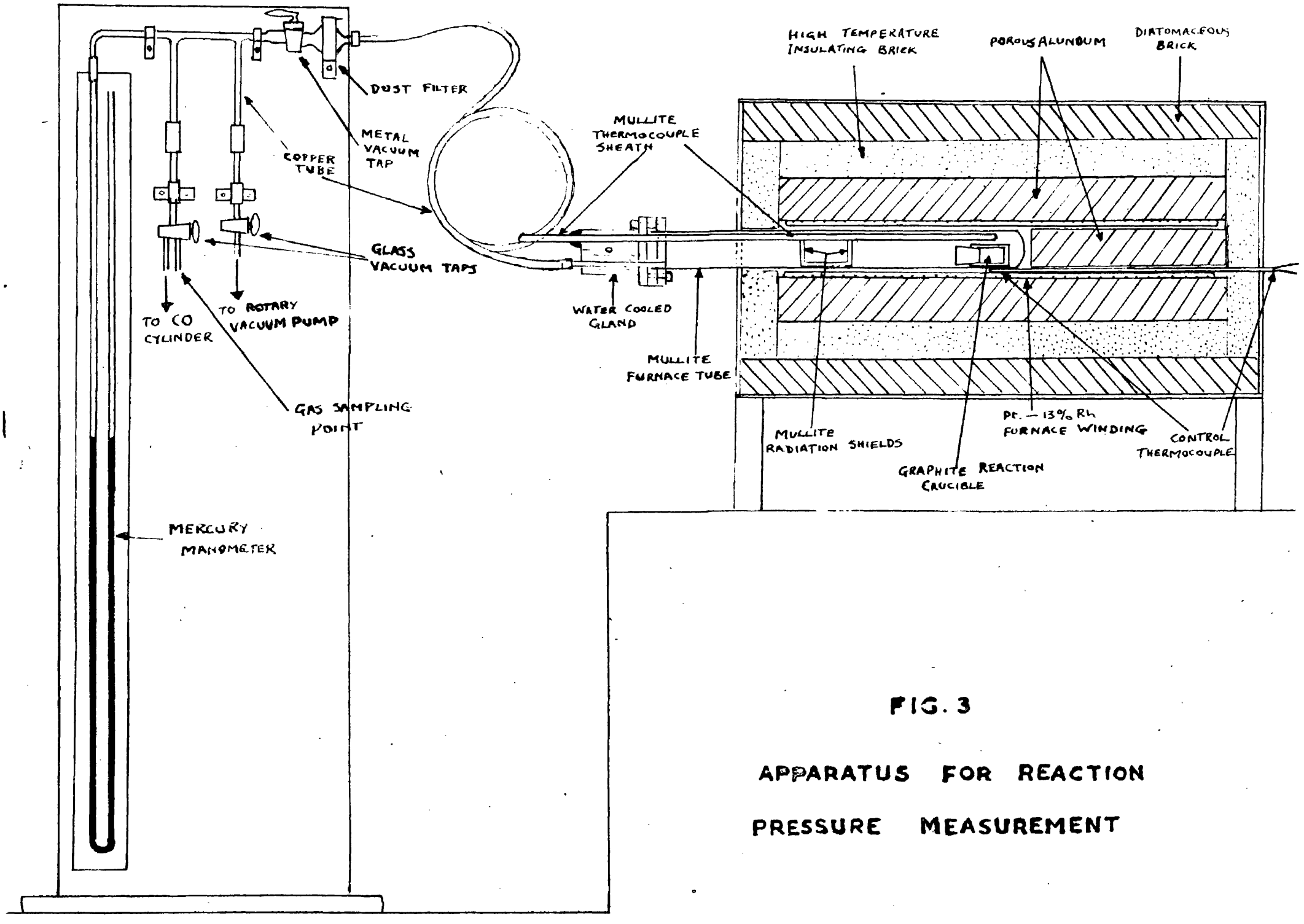


FIG. 3

APPARATUS FOR REACTION PRESSURE MEASUREMENT

the presence of leaks by the normal method of evacuating and allowing to stand, and all the tubes and joints had to be carefully tested before and after each run.

In the earlier stages of the work, most of the alumina tubes tried were either porous before use or developed pin-hole leaks during their first run. In alumina tubes which were closed at one end, failure usually occurred at the place where the hemispherical end had been joined on. Two recrystallised alumina tubes, open at both ends, were satisfactory from this point of view, but after their use for several runs it was found impossible to hold a vacuum at room temperature, even although no leaks could be detected by high frequency vacuum tester or by immersion in water under a positive pressure. The only possible reason for this was considered to be the formation of a surface active deposit on the inside of the tubes deriving from silicon monoxide vapour. Attempts were made to remove any such deposit by chemical treatment and ignition but the gas evolution from the tube appeared to have been thereby increased. These tubes were therefore discarded as it was considered that they might give rise to false results in the measurements of equilibrium pressures.

In later runs Morgan mullite tubes and thermocouple sheaths were used and precautions were taken to overcome errors due to active deposits. These tubes usually remained leakproof for 4 or 5 runs when used in the temperature range 1450-1550°C, and showed no sign of softening. Earlier lack of success with them was found to have been due to their use for degassing the graphite reaction crucibles. Reaction between graphite and

the mullite wall at low pressures was found to produce porosity in the area of contact in a few hours at 1500°C. This was avoided by resting the graphite crucible on an alumina plaque during the degassing operation.

(2) Temperature Measurement.

The temperature of the graphite crucible was measured by a Pt/Pt+13% Rh. thermocouple lying in the mullite thermocouple sheath whose end was level with the middle of the crucible. This thermocouple was checked several times at the melting point of palladium, and when contamination was likely to occur due to a leak in the thermocouple sheath the end of the couple was removed and the new junction was tested against a new thermocouple. The E.M.F. of the thermocouple was measured by a Cambridge Potentiometer, and a correction was applied for the temperature of the cold junction. Since the reactions investigated are very temperature sensitive, great care was necessary in the measurement of temperature to obtain reproducible results.

In earlier runs the furnace temperature was controlled manually by manipulation of the Variac transformer which controlled the voltage across the windings. In most of the later runs the temperature was controlled automatically by a Kelvin-Hughes electronic controller. The thermocouple used for the controller was situated along the winding tube. By this method the temperature of the crucible could be maintained at ±2°C of the desired value. The thermocouple along the furnace windings also served as a check on the accuracy of the inside thermocouple.

(3) Pressure Measurement.

In the final design of the apparatus as shown in Fig.3, little difficulty was experienced with leaks other than those in the tube and thermocouple sheath. The design of the water-cooled gland on the end of the furnace tube is shown in Fig.4. The copper tube spiral conferred flexibility on the coupling between the furnace tube and the manometer board.

In order to prevent dust and grit being carried into the vacuum taps on the manometer board a simple filter was installed, as shown in Fig.5.

The glass vacuum taps on the manometer board were connected to the copper tubes by poly-vinyl chloride tubing, the join being made by heating the copper and glass tubes and pushing the plastic tube over them. The manometer tube was joined by a cone and socket joint sealed with picene wax.

Carbon monoxide gas was introduced into the apparatus through one limb of the two-way tap on the board. The carbon monoxide was obtained from a cylinder. In most of the earlier runs it was stored in a gas-holder over water, but this led to contamination from dissolved oxygen and nitrogen in the water, and in all later runs the gas was taken straight from the cylinder. The cylinder gas analysed as 100% CO in the Bone and Wheeler apparatus, using absorption by ammoniacal cuprous chloride.

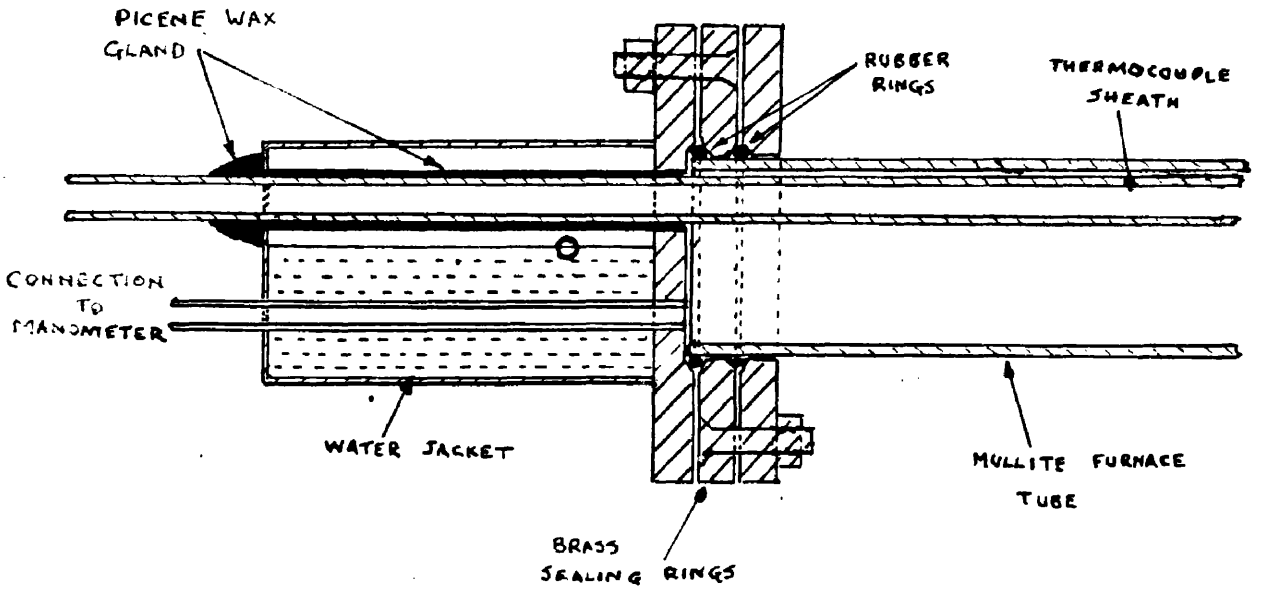


FIG. 4. WATER COOLED GLAND (HALF SIZE)

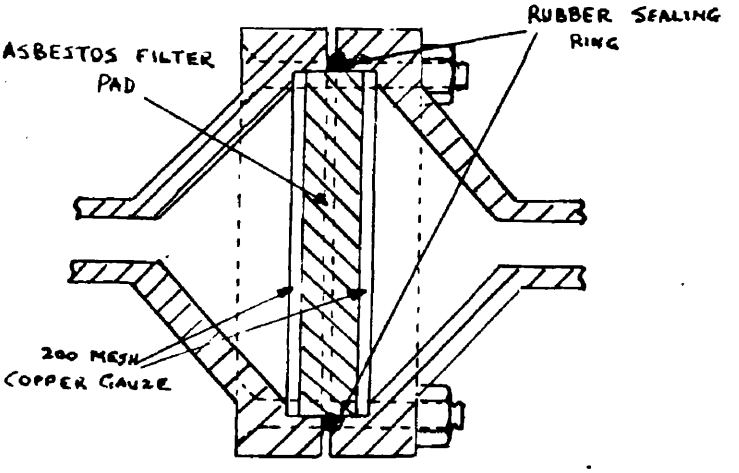


FIG. 5. DUST FILTER (FULL SIZE)

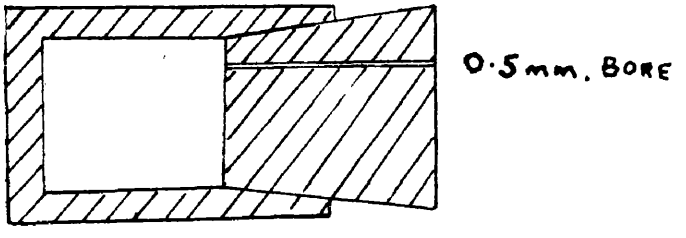


FIG. 6. GRAPHITE REACTION CRUCIBLE
(FULL SIZE)

Gas samples of the gas in the furnace tube were taken by attaching a 100 ml. gas sampling tube to the other limb of the two-way tap on the manometer board. The metal tap on the board was then closed and the sampling tube evacuated by the rotary pump. Gas was then admitted into the tube by opening the metal tap, and mercury was finally sucked into the sampling tube to reduce the pressure difference and so reduce the chance of leakage through the taps. Gas analysis was carried out in a Bone and Wheeler apparatus. In the earlier runs no measurable amount of carbon dioxide was found, and all later analyses were carried out for oxygen and carbon monoxide only, the residue being assumed to be nitrogen. Any oxygen present was assumed to be present due to leakage of air into the sample, and a correction was made to obtain the true gas composition. During the later runs when the experimental technique had improved, the oxygen content was either zero or very low (below 0.5 per cent) and the carbon monoxide was consistently above 97.5 per cent and usually 100 per cent.

(4) Crucibles.

The design of the graphite crucibles used is shown in Fig.6. The charges for the crucible were made up by pelletising the finely ground constituents at a pressure of 50 tons per square inch. In this form the crucible held a charge of about 8 gm.

Before use the crucibles were degassed by heating in vacuum for at least 3 hours at 1450°C. If the crucible was in contact with any siliceous material during degassing (such as the mullite furnace tube)

a skin of silicon carbide was formed near the point of contact. This skin was scraped off before the crucible was used to prevent errors due to uncontrolled oxidation of silicon carbide to gaseous silicon monoxide.

In order to cut down the slow absorption of air by the crucibles when not in use, they were stored in vacuum or in sealed glass tubes.

(5) Materials Used.

The three reactants used in this series of experiments were silica, silicon carbide and graphite. The silica was obtained from quartz sand of 99.3 per cent purity. This sand was of sufficient purity for the present experiments but as purer silica was required for making up slags it was finely ground in an agate mortar and then boiled with 50 per cent hydrochloric acid until free from iron. After this treatment the purity was 99.7 per cent. X-ray examination of the charge after an experimental run showed that the quartz had been almost wholly converted to cristobalite. The experimental results obtained should thus lie closer to the values for the reactions with β cristobalite than to those for β quartz.

Technical silicon carbide (which is hexagonal) was used, the finest grade designated as -700 mesh, being employed. Previously degassed Acheson graphite powder was the form of carbon used. Small amounts of impurities in these two constituents should have no effect on the equilibrium value reached.

(6) Blank Runs.

Early experimental results were not completely consistent, and so several blank runs were carried out to find out whether any part of the system other than the crucible contents could give rise to pressure changes in the tube. The blank runs were carried out first using recrystallised alumina tubes in the conditions existing after a run had been carried out. It was found that a "recovery" effect did take place in the tube whereby gas was evolved or absorbed in a direction such as to minimise any pressure changes made. For example if the tube was evacuated and then 1 atmosphere carbon monoxide was admitted, it was found that there was a decrease in pressure of up to 2 cm. Hg. within a period of 2 hours. Thereafter the pressure remained steady.

This effect was present both with and without a graphite crucible in the tube, although the recovery effect seemed greater in the former case. Some of it appeared to be due to porous alundum stools which had been used to cut down radiation and to reduce the volume of the reaction tube.

During the course of a run some silicon monoxide does escape through the capillary, and this appeared to give rise to deposits in the colder parts of the tube. Further away from the hot zone deposit was black and formed as a thin layer on the tube walls and radiation shields. It contained graphite and must have been formed either by carbon deposition or by the reaction:-

$$SiO(g) + CO = SiO_2 + C \quad \text{.....(1)}$$

Nearer the hot zone the deposit was more voluminous and of a white or bluish-white colour. X-ray examination by the powder method showed silicon carbide to be present (Fig.7 - X.1)*, and chemical analysis showed that silica was present exactly in the proportion expected if the reaction were :

$$3SiO(g) + CO = 2SiO_2 + SiC \quad \text{.....(2)}$$

As a new tube showed no recovery effect when tested in a blank run this effect must have been due to the presence of these deposits in the tube.

In order to minimise the recovery effect the porous alundum stools in the furnace tube were removed and replaced by radiation shields made from mullite tube. These radiation shields were cleaned before each run and the thermocouple and furnace tube were also scraped free of deposit.

* Cubic silicon carbide is the modification formed at temperatures below 2000°C(47), but no X-ray pattern of cubic silicon carbide was available with which to compare the patterns obtained in the other photographs. However, commercial silicon carbide, which is hexagonal, gives a pattern containing all the lines of cubic silicon carbide together with a large number of extra lines (No.X.3). The five strongest lines of cubic silicon carbide have d-spacings of 2.51, 1.54, 1.311, 0.888 and 0.837 Å, and the lines of these d-spacings have been marked on No.X.3. They can be seen to be also present in Nos. X.1, X.4, X.5 and X.7, but absent in X.6.

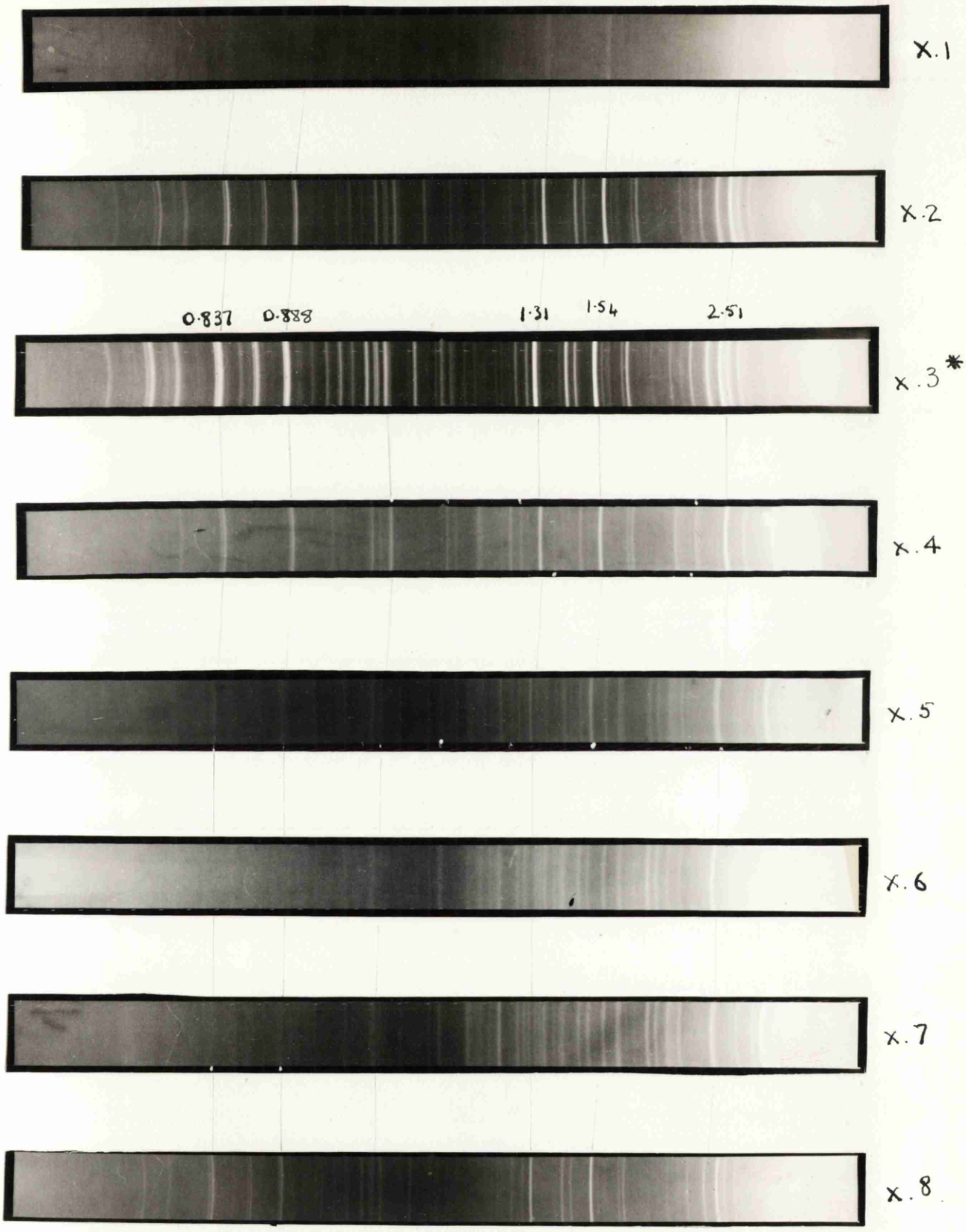


Fig.7 X-Ray Powder Photographs. Cu Kα radiation, 9 cm. Camera. (See footnote, page 38).

In addition to these measures, the possibility of errors due to absorption or desorption of gas by deposits in the tube was met by using long experimental runs. Inthis way time was allowed for the small amount of deposit present to come into equilibrium with the particular gas pressure in equilibrium according to the reaction being examined. Where reaction rates were found to be slow, as is the case with solid reactants, a reaction pressure determination took at least 5 hours, and many extended to over 24 hours.

Confirmatory evidence of the absorptive power of the deposits formed inside the furnace tube was obtained from the gas analyses. It was found that, if nitrogen was introduced into the tube the gas in the following run was high in nitrogen. A considerable amount of high temperature evacuation was necessary to eliminate such absorbed nitrogen.

In the final form of the apparatus the total effective volume of the reaction tube was found to be 162 c.c. with the crucible at 1500°C, and, the volume of the tubing to the left of the metal tap was 13 c.c.

(7) Experimental Procedure.

The exact experimental procedure used varied with the experiment being carried out. However, in general, the crucible was charged and the furnace was then heated up with the furnace tube connected to the rotary pump to remove any adsorbed extraneous gases from the tube. In runs where the charge contained silica and carbon the pump was switched off at about 1200-1300°C to prevent excessive formation of silicon monoxide.

Some carbon monoxide was then admitted to cut down further reduction of silica.

When the furnace temperature had reached the desired reaction temperature, the reaction pressure was measured whenever possible by approaching equilibrium from both the high and low pressure sides. The carbon monoxide was renewed occasionally, but excessive pumping out at high temperatures was avoided, as it was found to give rise to three adverse effects, viz.,

(a) Excessive evaporation of silicon monoxide from the reaction crucible. This silicon monoxide vapour then condensed on the colder areas of the tube, where it was re-oxidised on the admission of fresh carbon monoxide, presumably according to the reaction:-

$$3SiO + CO = 2SiO_2 + SiC \quad \text{.....(2)}$$

(b) Reaction between the outside of the crucible and the wall of the mullite furnace tube according to the equation:-

$$SiO_2\text{(mullite)} + 3C = SiC + 2CO \quad \text{.....(3)}$$

This reaction resulted in the formation of a hard silicon carbide skin on the crucible which may have been gradually re-oxidised by carbon monoxide to form gaseous silicon monoxide or solid silica.

(c) Excessive pumping out is likely to give rise to a large "recovery" adsorption effect on the admission of carbon monoxide.

Normally the experimental procedure was to pump out the tube with the stopcocks fully open for a few seconds only at high temperatures. Longer exhaustion was always found to give rise to a temporary decrease in carbon monoxide pressure when the gas was re-admitted to the tube.

(8) Experimental Results.

(a) Silicon Carbide runs.

Two runs were carried out using a charge of silicon carbide in the crucible. The tube used for both runs was of recrystallised alumina.

Run 1. At 1500°C, and with initial values of p_{CO} ranging from 0.3 atm. to 0.6 atm., a gradual decrease in carbon monoxide pressure was observed. In the longest run reaction was found to have virtually ceased after 24 hours, the final pressure reached being 0.286 atm. CO, after an absorption corresponding to a pressure decrease of 0.22 atm.

Run 2. Pressure/time curves for this run are shown in Fig.8. This run differed from Run 1 in that the initial pressure was higher. On heating up, 1 atmosphere of CO was admitted at 1300°C and a considerable absorption took place between 1300°C and 1500°C, resulting in an initial pressure of 62 cm. Hg., as shown in Fig.8. While the temperature remained steady at 1500°C a further gradual absorption took place, but when the pressure was reduced to 41 cm. Hg., by pumping out some gas, there was a rapid evolution of gas inside the tube. This pumping out was repeated, and the same result was obtained. The pressure was then increased again by the admission of more CO and the reaction was allowed

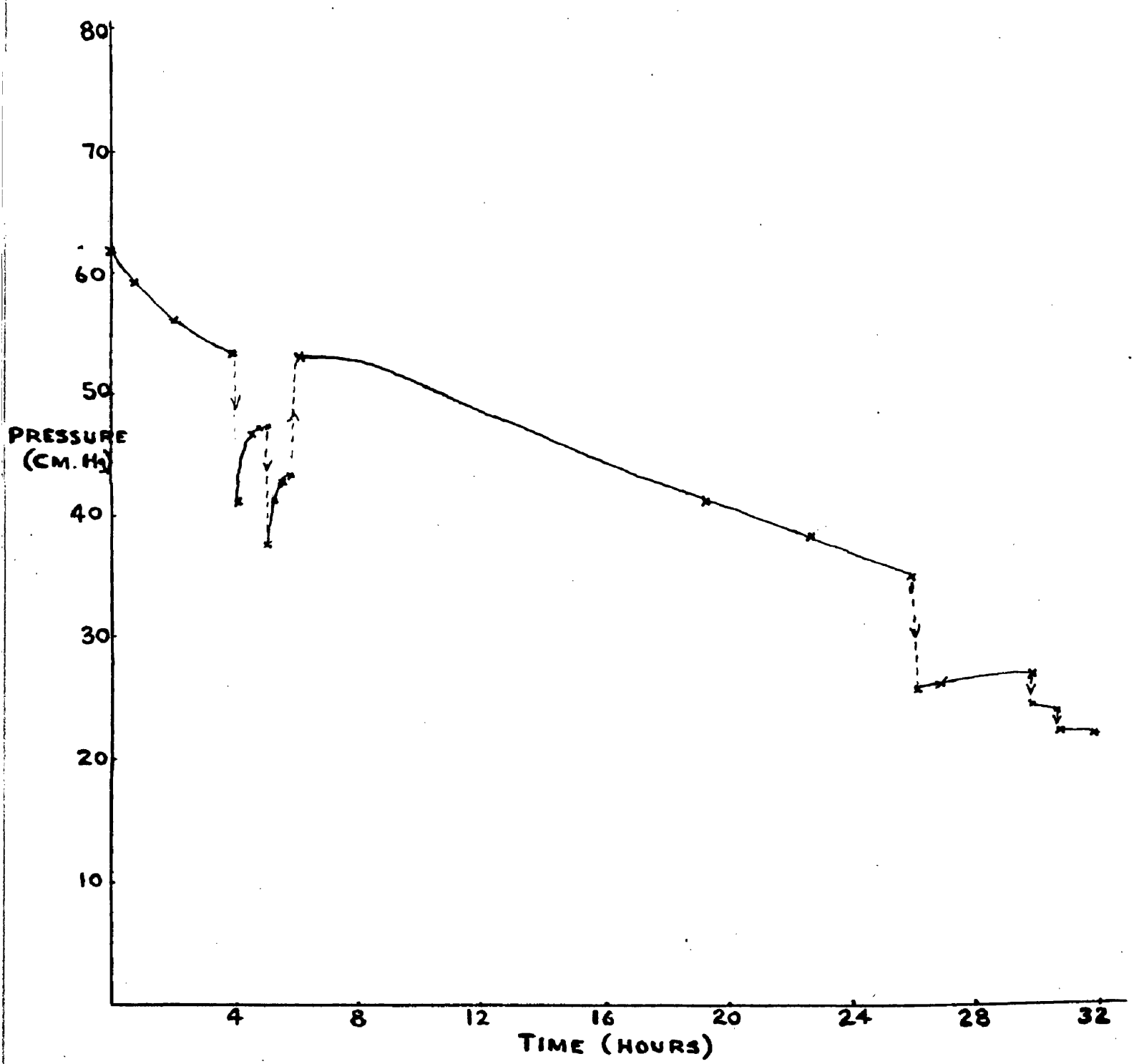


FIG. 8 SILICON CARBIDE RUN No. 2.

to proceed overnight. As is shown by Fig.8 a further gradual absorption of carbon monoxide took place, and the probable shape of the pressure/time curve has been indicated.

Reference to the theoretical discussion of this system on page 26 shows that the results obtained correspond to the formation of some solid oxidation product of silicon carbide which is stable at carbon monoxide pressures of more than about 50 cm. Hg. at 1500°C. This compound could either be silica, in which case some of the thermodynamic data used in the calculations in Chapter 3 must be wrong, or some intermediate compound. By lowering the pressure the small amount of solid oxidation product (formed at pressures above 50 cm. Hg.) must have been consumed by some reaction such as

$$SiO_2 + C = SiO(g) + CO \quad \text{.....(1)}$$

This would account for the gradual absorption of carbon monoxide which took place in the latter stages of the run, as this would correspond to diffusion controlled oxidation of silicon carbide to gaseous silicon monoxide:-

$$SiC + CO = SiO(g) + 2C \quad \text{.....(3)}$$

If silicon monoxide formed by this reaction condensed in the tube or reacted to form some solid compound, a gradual decrease in total pressure would be expected, as was noted in Chapter 3, page 30.

Confirmation of this interpretation of the results was obtained by examination of the contents of the reaction tube after the run. An X-ray powder photograph of the contents of the crucible was taken, and this revealed only silicon carbide (Fig.7 - X.2). In addition it was found

that a considerable amount of deposit had been formed inside the furnace tube. This deposit was found not to change in weight when ignited in air (solid silicon monoxide would probably have increased in weight due to oxidation), and when treated with hydrofluoric acid a loss in weight of 75 per cent took place. An X-ray powder photograph was taken of the deposit, and is shown in Fig.7 - X.1. Comparison of this photograph with that of commercial silicon carbide (No.X.3) shows that the deposit contains silicon carbide. The reactions which would give a deposit containing some silicon carbide and 75 per cent silica are:-

$$SiC + CO = SiO(g) + 2C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

in the crucible, and

$$3SiO(g) + CO = 2SiO_2 + SiC \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

in the colder parts of the furnace tube. The weight of the deposit was found to be sufficient to account for all the carbon monoxide consumed, assuming reactions (3) and (2) to be taking place.

As is shown by Fig.8, a small increase in reaction pressure was also obtained at a later stage in the run when some carbon monoxide was removed by pumping out. This increase can be seen to be much slower and smaller than that obtained at higher pressures, and was probably due to the "recovery" effect, since the precautions against this effect given on page 48, had not been taken at this early stage in the work.

After completing this run at 1500°C, the temperature was lowered to 1450°C, the initial pressure being 23 cm. Hg (or 0.3 atm.). A further decrease in pressure was obtained at this temperature over a period of 24 hours.

(b) Silica and Carbon Runs.

Seven runs were carried out using a charge consisting of a finely ground mixture of silica and graphite. In the first 3 runs the charge was compacted in the crucible by hand, and in the last 4 runs the charge was pelletised at 50 tons per square inch. In order to prevent the formation of silicon carbide during heating up, the furnace tube was not evacuated above 900°C, about 1 atmosphere of carbon monoxide being admitted at this temperature.

The main purpose of these runs was to investigate the possibility that silica might be reduced by carbon to some solid compound other than silicon carbide. This type of system would lead to a pressure/temperature diagram of the type proposed by Brunner(43), as shown in Fig.2. If this type of system were correct silica and carbon should react at a pressure higher than that of the calculated SiO_2-SiC-C equilibrium to form a third solid compound.

The results of these runs will be discussed in detail later in the light of the results of the SiO_2-SiC-C runs. At this point it may be noted, however, that they tended to support the simple type of Si-C-O system depicted in Fig.1. Denoting theequilibrium carbon monoxide pressure for the reaction:

$$SiO_2 + 3C = SiC + 2CO \quad \text{.....(5)}$$

by p_{CO} eq., it was found that, at pressures above p_{CO} eq., slow diffusion-controlled reduction to silicon monoxide took place, while below p_{CO} eq., reduction to silicon carbide took place.

(c) Silica-Silicon Carbide-Carbon Runs.

In these runs it was found possible to reach a definite equilibrium pressure, approaching from both the high- and low-carbon monoxide pressure directions by the normal experimental procedure, using a mixture containing equal proportions of the three constituents by volume. The results obtained by this method were not at first completely consistent among themselves but without exception the reaction pressures measured were much lower than the calculated values of p_{CO} and p_{SiO} given in Tables I and III had led one to expect. A large number of runs were carried out at 1450°C and 1500°C to determine the cause of the small inconsistencies, and also to establish with certainty the reaction to which the measured pressures referred. These experiments will be dealt with now.

(i) Experimental Consistency.

At the time when these experiments were being carried out, considerable difficulty was experienced in obtaining a pure carbon monoxide atmosphere in the furnace tube. Even in cases where the whole tube assembly had been tested under water before and after the run and found to be leak tight, a considerable percentage of nitrogen was often found to be present in the furnace gas. Repeated pumping out and renewal of carbon monoxide was not considered advisable due to the effects noted on page 40, and in addition some nitrogen had been introduced into the tube with the carbon monoxide due to the latter having been stored over water.

A connection appeared to exist between the purity of the furnace atmosphere and the measured partial pressures of carbon monoxide. This

is clearly shown from the results given in Table V.

TABLE V.

Partial pressures of carbon monoxide measured in SiO_2-SiC-C runs.

1450°C		1500°C	
P_{CO}	%CO	P_{CO}	%CO
0.474	80.4	0.723	98.6
0.450	89.5	0.719	76.6
0.419	94.8	0.715	81.8
0.376	100	0.736	85.7
0.414	88.2	0.764	84.1
0.441	91.2	0.793	89.3
0.390	97.8	0.729	100 *
* Solid plug crucible		0.716	100 *

It can be seen that the measured values of p_{CO} are quite consistent in the cases where the carbon monoxide content is greater than 97 per cent, but that the values of p_{CO} are in most cases greater where the gas is less pure.

An attempt was made to discover if there was any chemical reason for this effect by investigating the effect of nitrogen on silicon carbide contained in a carbon crucible. The results were difficult to interpret due to the simultaneous generation of carbon monoxide by the reaction between the crucible and the mullite furnace tube, but it appeared that some absorption of nitrogen had taken place in the tube. The experiments were discontinued as they were found to give rise to high nitrogen contents in subsequent runs carried out in the same tube (for example the gas sample shown in Table V containing 76.6% CO was the first to be drawn after a nitrogen run).

A second possibility was that the effect was caused by differences between the gas composition inside and outside the crucible. A fuller discussion of this effect will be given later, but it appeared unlikely from an examination of the results that this could be the sole explanation. In one or two cases the high nitrogen content and high value of p_{CO} may have been due to a slight air leakage, but this was not the case in the great majority of the runs quoted.

When the experimental technique had improved it was found possible to keep the nitrogen content of the furnace atmosphere below 2 per cent, and a high degree of consistency was then obtained in the measured reaction pressures.

(ii) Experimental Reaction.

The most obvious interpretation of the reaction pressures measured in these runs is that they refer to the reaction:-

$$SiO_2 + 3C = SiC + 2CO \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

However, since the pressures measured are so much lower than those predicted by calculation from apparently well-founded data, the possibility that this might not be the case was examined. Two causes appear to be possible, viz:-

(a) The diffusion of silicon monoxide gas from the crucible had disturbed the equilibrium.

(b) A third solid compound in the Si-C-O system was stable under the experimental conditions.

Both possibilities have been treated in the theoretical examination of this system in Chapter 3. In the former case it was noted that a low carbon monoxide pressure might be reached if the reaction

$$SiC + CO = SiO(g) + 2C \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

were very much more rapid than the two reactions

$$SiO_2 + C = SiO + CO, \text{ and}$$

$$SiO_2 + 3C = SiC + 2CO$$

It was also shown that if this were the case the difference between the measured value of p_{CO} and p_{CO} eq. could be reduced by decreasing the rate of diffusion of silicon monoxide and by increasing the reaction rates by improving particle contact.

The effects of both these changes were investigated. Reaction pressures were measured using a crucible with a solid plug, relying on gas diffusion between the crucible wall and the plug to equalise the pressures inside and outside the crucible. In addition the charge, for the first time in this series, was pelletised. The two results obtained in this way are marked by an asterisk in Table V, and it can be seen that they agree excellently with the best of the results obtained with a capillary opening in the crucible and a lightly compacted charge. It would thus appear that the lowness of the pressures measured cannot be attributed to silicon monoxide diffusion from the crucible.

It may be noted in support of this conclusion that the runs carried out with silica-carbon and with silicon carbide charges did not indicate any wide difference in the rates of the two reactions:-

$$SiO_2 + C = SiO(g) + CO \quad \text{.....(1)}$$

$$\text{and } SiC + CO = SiO(g) + 2C \quad \text{.....(4)}$$

Pelletising of the charge was used in all the succeeding runs in which equilibrium pressures were measured at 1400°C, 1550°C and 1580°C. Solid plug crucibles were also used occasionally and appeared to have no effect on the results obtained.

The presence of a third solid compound, stable at high temperatures only, would separate the system into the areas shown in Fig.9, assuming the compound to be intermediate, in oxidising and reducing power between silica and silicon carbide. It is possible that a system such as this in which a mixture of silica, carbon and silicon carbide would be metastable above T_1, might give rise to low reaction pressures along the line OB. If this were the case it should be possible to measure a series of reaction pressures along the line OA by preparing a mixture with a large excess of silica.

This has been attempted by using a mixture of silica and carbon and holding the gas pressure sufficiently low to form a little solid reduction product. When this had been done it was found possible to measure an equilibrium pressure for the mixture, approaching from both above and below in the usual way. The measured equilibrium pressures obtained in this way are shown in Table VI. They can be seen to agree well with measurements made using changes containing a large proportion of silicon carbide.

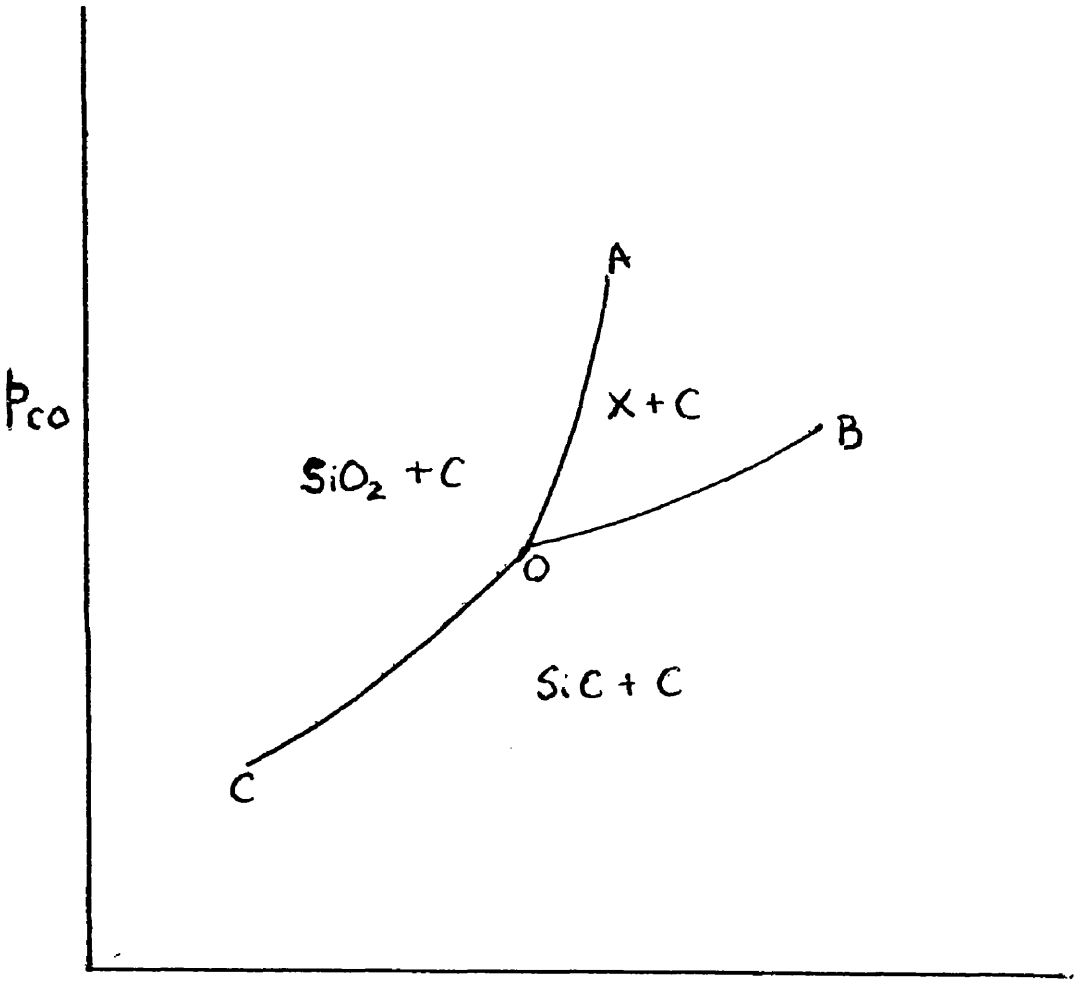


Fig.9.

Type of Pressure/Temperature Diagram obtained if there is a compound X, stable only at high temperatures.

TABLE VI.

Measured reaction pressures for SiO_2 + C mixtures containing a small amount of silicon carbide.

1450°C.		1500°C.	
P_{CO}	%CO	P_{CO}	%CO
0.415	97	0.714	97.5
0.366	100		

In runs where silica-carbon mixtures had not been held at pressures low enough to form silicon carbide, a slow upward drift in pressure was always obtained. This corresponds to diffusion controlled reduction of silica to gaseous silicon monoxide, as discussed on pages24/25. An example of this pressure change is shown later, in Fig.10.

In one SiO_2 + C run at 1550°C the tube was pumped down to 0.5 cm. Hg five times and allowed to generate gas up to atmospheric pressure. The pressure was then raised to 1.35 atm. and carbon monoxide was slowly absorbed down to a pressure of 1.1 atm., although the equilibrium pressure at 1550°C with SiO_2-SiC-C charges had been found to be 1.27 atm. The reason for this is believed to have been the formation of silicon carbide at the point of contact between the crucible and the mullite tube. An X-ray of hard powder scraped from the crucible at this point is shown in Fig.7-X.4, clearly showing the presence of silicon carbide. Oxidation of this silicon carbide to silicon monoxide by carbon monoxide could give rise to a low reaction pressure since diffusion is unrestricted at this point. In the other silica-carbon runs quoted less vigorous reaction had taken place and no hard skin was apparent on the crucible.

An X-ray powder photograph of the crucible contents from this run is shown in No.X5. From a comparison with No.X3, silicon carbide can clearly be seen to be present.

From the present results it would appear that at 1500°C silicon carbide should only be formed from silica and carbon at pressures below 0.72 atm., whereas previously the thermodynamic data indicated a value of 1.5 atm. Two experiments were carried out in an attempt to decide between the two values. A small silica-carbon pellet was held at a pressure of 1 atm. carbon monoxide at 1500°C for 46 hours in a standard graphite crucible. The X-ray powder photograph is shown in No. X6, and gives no indication of the formation of silicon carbide as would have been expected from the previous data. This was in contrast to a previous run carried out over a shorter period of time or a pressure slightly below 0.7 atm. (See Fig.7 No.X.7). In the second experiment silicon carbide in the standard graphite crucible was held for 33 hours at 1500°C in 1 atm. pressure of carbon monoxide, but the result of this run was negative, no silica pattern being visible on the X-ray photograph - No. X8.

Even although the result of this last run was negative it was considered that the evidence that the pressures measured refer to the true SiO_2-SiC-C equilibrium was overwhelming. Measurements were therefore taken over as wide a range of temperatures as possible, using silica-silicon carbide-carbon mixtures. The temperature limits were set by the slow reactions and small pressures at low temperatures, and by the tube and furnace limits and the high pressures at high temperatures. These factors limited the measurements to the range from 1400°C to 1580°C.

Pressure/time curves for these runs are shown in Figs.10 and 11 and the values of the equilibrium pressures were taken as follows:-

1400°C. The gas in these runs was only about 96% CO and this probably accounts for the gap between the two curves. The crucible used had a solid plug and this must accentuate the effect whereby the gas in the crucible is constantly enriched with carbon monoxide when equilibrium is approached from the low-pressure side, and enriched with nitrogen when approaching from the high pressure side. For this reason the best value has been taken to be that obtained from the lower curve, assuming the gas in the crucible to be 100 per cent carbon monoxide. This leads to a reaction pressure of 0.216 atm.

1450°C. A similar effect is apparent here, being especially marked since the only long approaches from above were accompanied by carbon monoxide content in the region of 90 per cent. The most reliable run appeared to be that in which the pressure remained completely constant at 0.376 atm. for 24 hours, and in which the gas was found to be 100 per cent. carbon monoxide. The other curves tend to indicate a slightly higher value, however, and the best value has been taken to be 0.382 atm. The curves obtained from silica-carbon mixtures in which a small amount of silicon carbide had been allowed to form are also shown.

1500°C. The two long approaches with high purity gas compositions appear to establish the equilibrium pressure accurately, and it has been taken as 0.723 atm. The pressure change obtained with a fresh silica-carbon mixture is also shown on Fig.10.

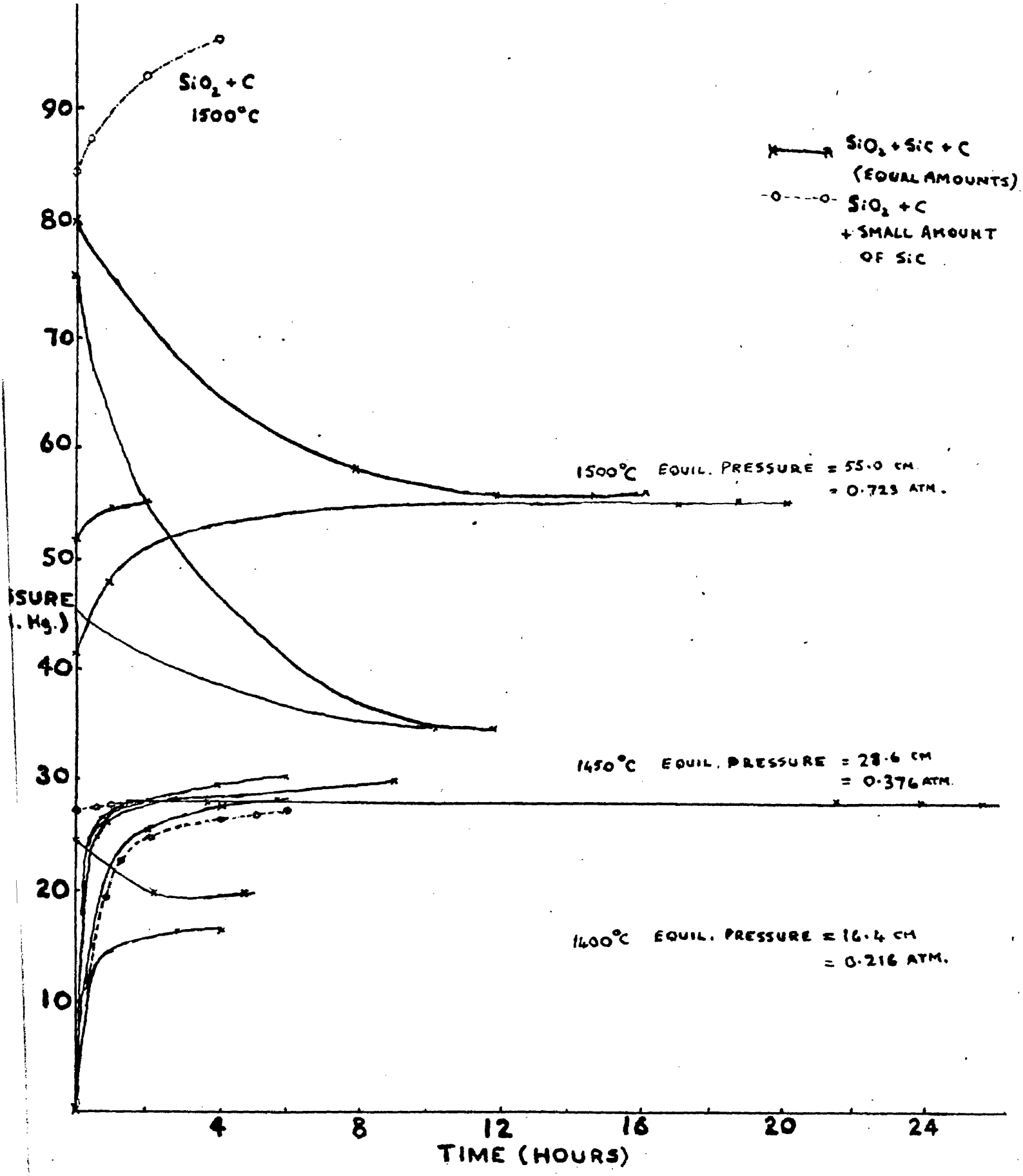


FIG. 10. REACTION PRESSURE MEASUREMENTS FOR SiO_2-SiC-C MIXTURES

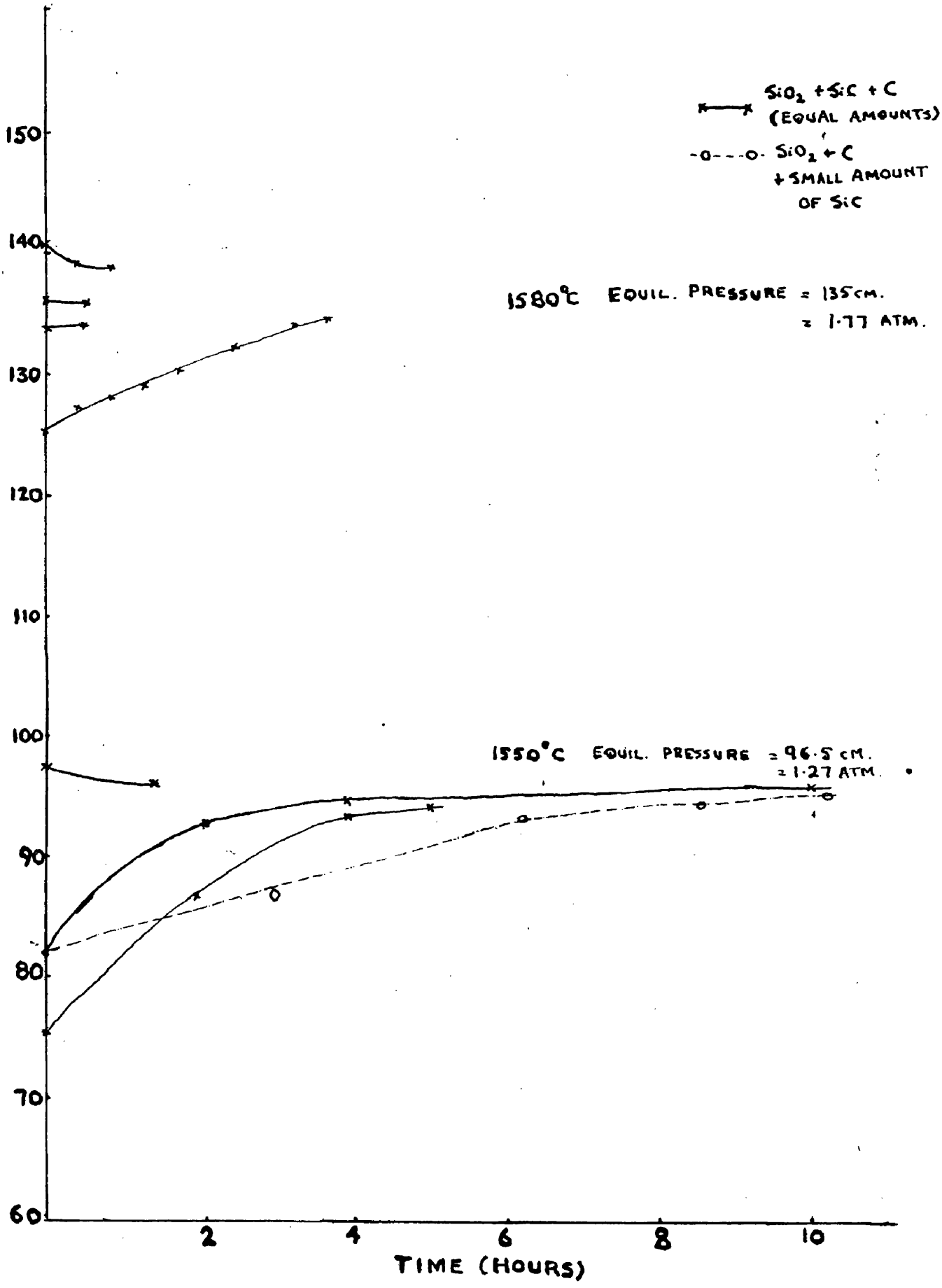


FIG. 11. REACTION PRESSURE MEASUREMENTS FOR SiO_2-SiC-C MIXTURES

1550°C. Although the only approach from the high pressure direction is rather short, this value is also quite well established at 1.27 atm.

1580°C. The difficulties of working so near the limits of the apparatus necessitated the use of fairly short runs at this temperature, but this is partly compensated by the higher reaction rates, and the pressure of 1.77 atm. was consistently indicated.

(9) Discussion of Results.

Comparison of the results with the calculated values of p_{CO} and p_{SiO} given in Tables I and III indicates a wide discrepancy, and this must be due to an error in the thermodynamic data on which the calculations were based. While the free energy of formation of silica may be slightly in error it is considered that the greater part of the discrepancy must be attributed to an error in the free energy of formation of silicon carbide. The determination of the heat of formation of silicon carbide is very difficult due to its unreactive nature, and although such a large error in the determination by Humphrey, Todd, Coughlin and King(25) appeared unlikely, this quantity is the one most open to doubt.

Taking the silica free energy to be correct it can be seen that the values of K for the reaction $SiO_2 + C = SiO(g) + CO$ in Table II should still hold good. Using the measured reaction pressure as an approximation for p_{CO}, the equilibrium value of p_{SiO} can be calculated from the given values of $p_{CO} \times p_{SiO}$ at each temperature, and these

values are shown in Table VII. Since the measured reaction pressure is $p_{CO} + p_{SiO}$, the carbon monoxide pressure of the reaction:-

$$SiO_2 + 3C = SiC + 2CO \quad \text{.....(5)}$$

can then be obtained by subtraction. This value of p_{CO} has been plotted against temperature in Fig.12, and $\log_{10} p_{CO}$ has been plotted against $1/T°K$ in Fig.13.

TABLE VII.

T°C	$p_{CO} + p_{SiO}$	p_{SiO}	p_{CO}	$\log_{10} pCO$	$1/T°K \times 10^3$
1400	0.216	0.009	0.207	-0.684	0.5977
1450	0.376	0.016	0.360	-0.444	0.5805
1500	0.723	0.029	0.694	-0.159	0.5640
1550	1.27	0.039	1.23	+0.090	0.5486
1580	1.77	0.060	1.71	+0.233	0.5396

The latter plot indicates that there is a straight line relationship between $\log_{10} p$ and $1/T°K$ and this lends support to the conclusion that a true equilibrium for the system has been reached. The equation of this line is:-

$$\log_{10} p_{CO} = 8.926 - \frac{16,110}{T}$$

since $K_5 = p_{CO}^2$, $\log_{10} K_5 = 17.852 - \frac{32,220}{T}$

since $\Delta G°_5 = - RT \ln K_5$

$$\Delta G°_5 = 147,400 - 81.68\ T$$

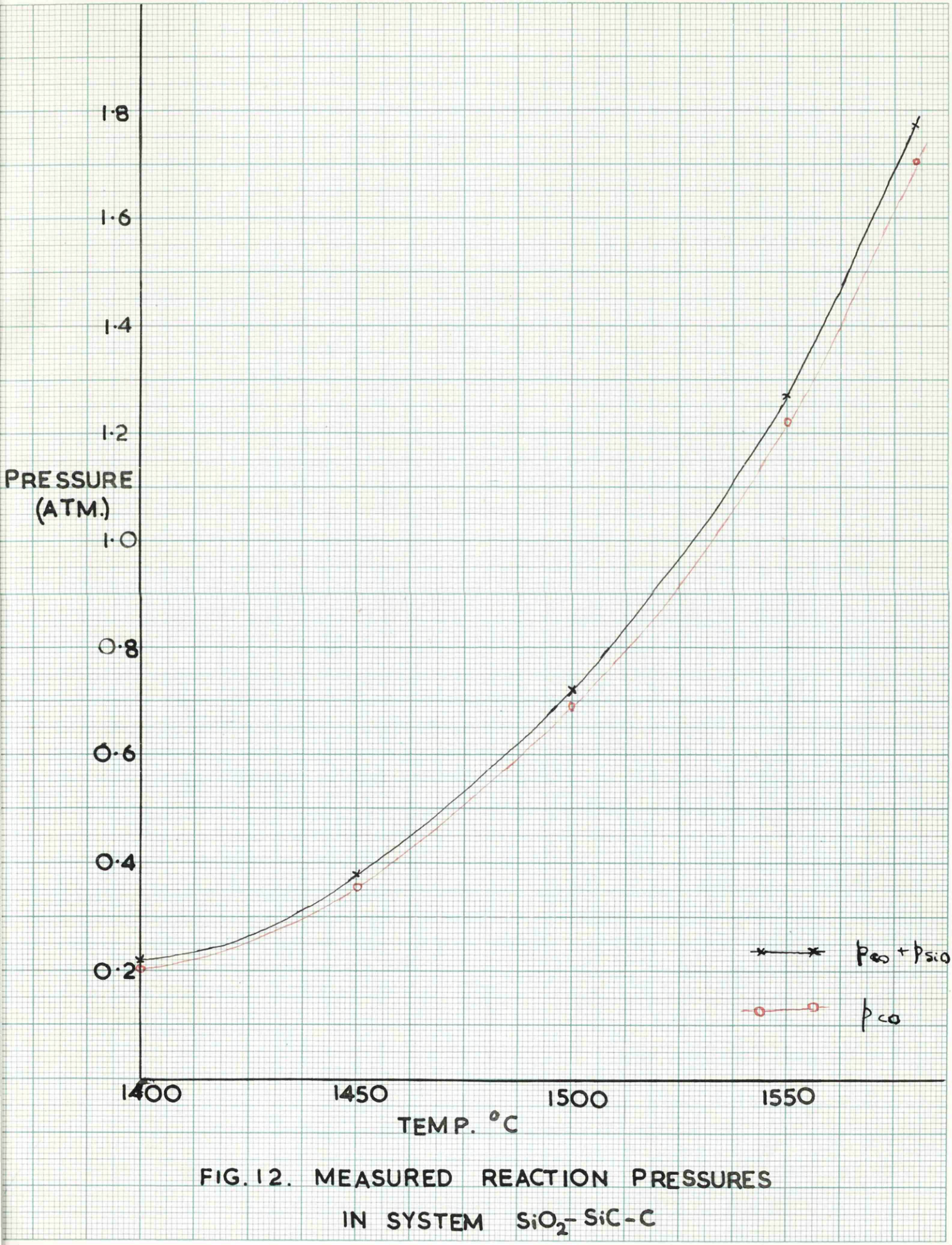


FIG. 12. MEASURED REACTION PRESSURES IN SYSTEM SiO_2–SiC–C

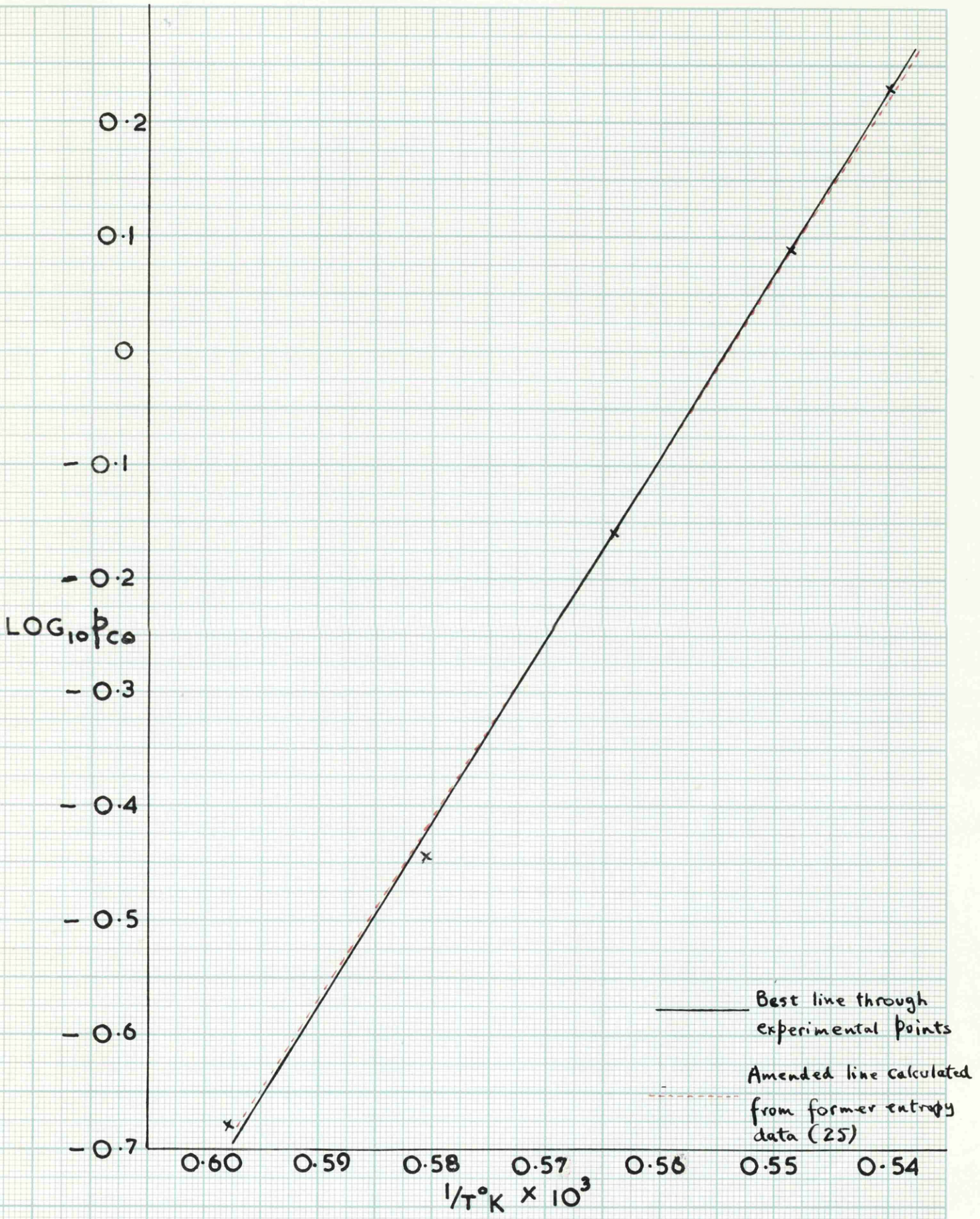


FIG.13. MEASURED CO PRESSURES FOR REACTION :-

$SiO_2 + 3C = SiC + 2CO$

Taking the free energies of formation of silica and carbon monoxide given previously, the following equation is obtained for the free energy of formation of silicon carbide.

$$Si(l) + C(graphite) = SiC$$

$$\Delta G^\circ = -15,200 + 6.02\ T$$

compared with the equation obtained by Humphrey et al(25):-

$$\Delta G^\circ = -24,700 + 8.3T$$

It is considered that the equation derived above does represent accurately the free energy of formation of silicon carbide in the experimental range of 1400-1580°C. However, in view of the fact that the value of the entropy term in equation of Humphrey et.al. is so well established by their own heat capacity measurements and those of Kelley(30), it is probable that this term is accurate. In consequence some readjustment of the present equation may be required to bring it in to alignment with this value. Such readjustment leads to the equation:-

$$\Delta G^\circ_{SiC} = -19,240 + 8.3T$$

The effect of this change on the experimental curve for $\log p_{CO}/ \frac{1}{T}$ has been calculated, and is shown in Fig.13. As can be seen it is small enough to be within the experimental error.

CHAPTER 5.

THE MEASUREMENT OF SILICA ACTIVITIES IN SLAGS.

(1) Theoretical Considerations.

The necessary data is now available to make possible the determination of silica activities in liquid silicate slags by measuring the reaction pressure of the reaction:-

$$SiO_2(slag) + 3C = SiC + 2CO \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

For this reaction $K_1 = \frac{p_{CO}^2}{a_{SiO_2}}$, and the value of K_1 may be obtained from the equation derived in Chapter 4, page 54, viz.,

$$\log_{10} K_1 = 17.852 - \frac{32,220}{T}$$

In the present experiments measurements were made at 1450°C, 1500°C and 1550°C, and the values of K_1 at these three temperatures are as follows:-

	1450°C	1500°C	1550°C
K_1	0.140	0.482	1.51

To obtain the value of p_{CO} from the measured reaction pressure it is necessary to know the partial pressure of silicon monoxide. This may be obtained most easily from the equilibrium:-

$$SiC + CO = SiO(g) + 2C \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

for which $K_2 = \frac{p_{SiO}}{p_{CO}}$

Using the free energy of silicon carbide derived in the previous Chapter it is found that:-

$$\Delta G_2^\circ = 6,960 + 2.88\ T$$

$$\text{and } \log_{10} K_2 = -0.630 - \frac{1,520}{T}$$

From this equation the values of K_2 at the working temperatures have been calculated:-

	1450°C	1500°C	1550°C
K_2	3.1×10^{-2}	3.3×10^{-2}	3.44×10^{-2}

Since p_{SiO} is a small fraction of p_{CO}, the value of $p_{CO} + p_{SiO}$ can be used in place of p_{CO} in making use of these values of K_2 without introducing any significant error. This enables p_{SiO} to be calculated with sufficient accuracy from the total reaction pressure. The carbon monoxide pressure is then obtained by subtracting p_{SiO} from the total pressure, and the activity of silica may then be calculated from the values of K_1 given above.

This method of measurement of silica activities is confined to slags in which silica is the most easily reducible oxide. Such oxides as FeO, MnO and P_2O_5 are thus excluded. In the present experiments the only other constituents present have been lime and alumina. It is possible to calculate approximately the carbon monoxide pressures of the two reactions:-

$$CaO + 3C = CaC_2 + CO \quad \text{.....(3)}$$

and $$Al_2O_3 + 9C = Al_4C_3 + 6CO \quad \text{.....(4)}$$

using the free energy data of Richardson(44) and Richardson and Jeffes(45). At 1500°C the equilibrium carbon monoxide pressure of reaction (3) is about 5 mm. Hg, and of reaction (4) about 0.5 mm.Hg, so that neither is likely to interfere with the main reaction being studied since all the reaction pressures measured were above 60 mm. Hg.

(2) Experimental Procedure.

The reaction pressure measurements were carried out in the same apparatus as was employed for the experiments on solid silica. The charge for each run consisted of 5-6 gm. of powdered slag and about 1 gm. each of graphite and silicon carbide powder. This powder was mixed by grinding lightly in a mechanical agate mortar for 1-2 minutes. It was then pelletised at 50 tons/square inch and in this form the whole charge could be contained in the graphite crucible.

(3) Slag Composition.

After a run the charge still consisted of a finely divided mixture of slag, carbon and silicon carbide, although in some cases molten slag had coalesced into visible globules. No method of sufficient accuracy could be devised to analyse this mixture and it therefore has been necessary to analyse the slag before use in a run, and to control the run in such a way as to prevent large changes in slag composition due to excessive reaction in one direction or another.

Master slags were made up by first weighing out the requisite amounts of Analar calcium carbonate and alumina and purified silica and then roasting the mixed powder at 1000°C for 2 hours to drive off carbon dioxide. The powder was melted in a graphite crucible by means of a high frequency induction furnace. The melted slag was crushed in a percussion mortar and finally ground in an agate mortar and analysed for silica, alumina and lime by the usual methods.

Two series of slags were investigated, viz., lime-silica slags and lime-alumina-silica slags containing 20 per cent alumina. The lime-silica and lime-alumina-silica phase diagrams are shown in Fig.14 and 15 together with the slag compositions examined. The master slag compositions have been indicated on the diagrams. Compositions at intermediate points were made by mixing the requisite amounts of master slags. Values of N_{SiO_2} in the liquid were calculated from the analyses in the case of slags which were completely liquid, and from the phase diagram for slags which were only partially molten at the reaction temperature.

The analysed alumina contents of the lime-silica slags are higher than those expected from the purity of the raw materials used, and the reason for this is not known. In slags which are completely liquid the amount of alumina present should have only a slight effect on the silica activities but in addition it does alter the composition of the liquid in semi-solid slags by a small amount. In all cases N_{SiO_2} in the liquid has been calculated taking the alumina content into account.

In order to measure the equilibrium pressure it is necessary to allow some reaction to take place, and any reaction produces a change in composition of the slag. The effective volume of the reaction space under working conditions is about 175 cc.(i.e., 175 c.c. of gas, as measured at N.T.P., would exert a pressure of 1 atmosphere if introduced into the reaction space). A change of pressure of 20 cm. Hg is thus equivalent to the consumption or production of 0.062 gm. silica,

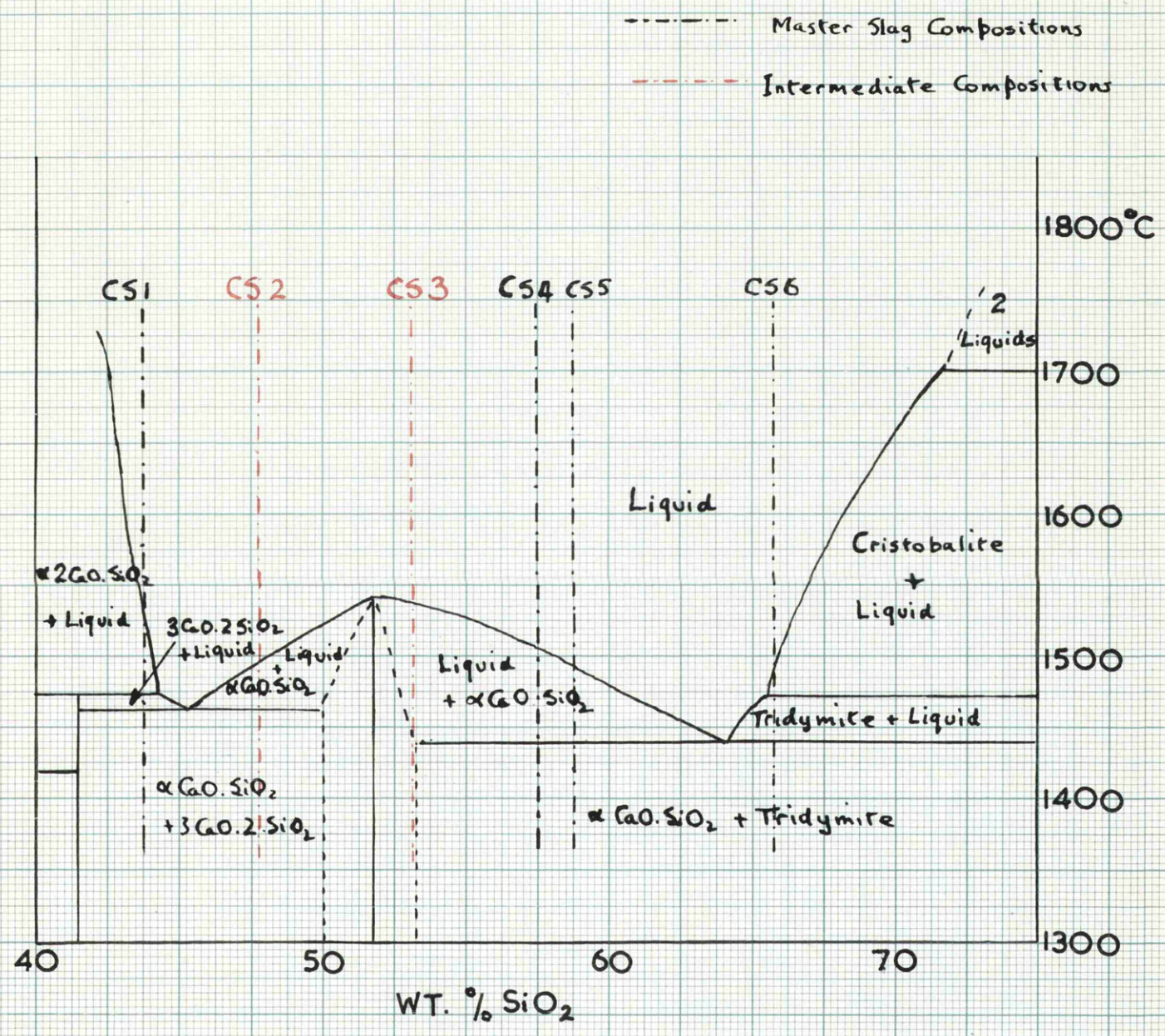
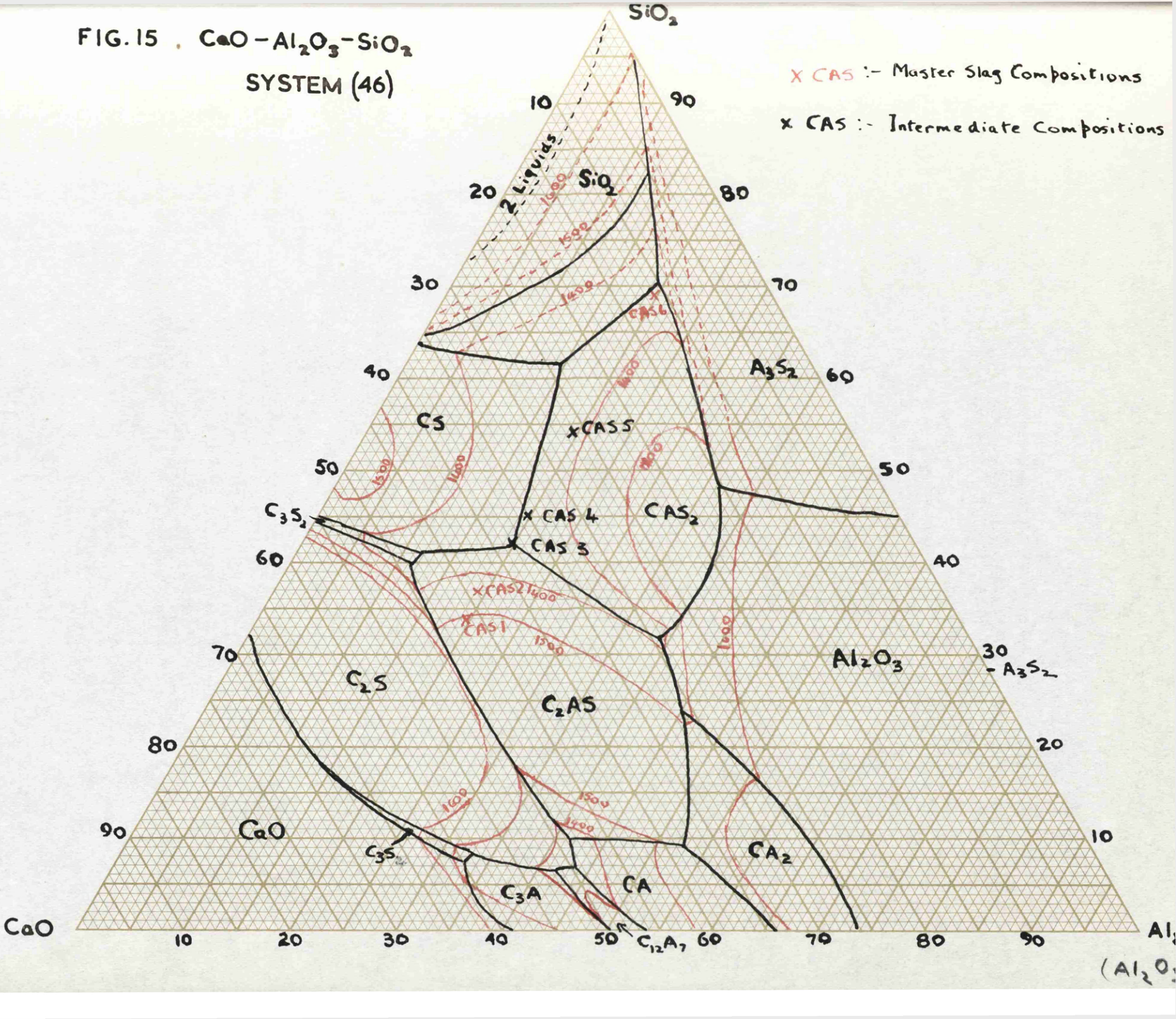


FIG. 14. CaO – SiO_2 SYSTEM (46)

FIG. 15 . $CaO-Al_2O_3-SiO_2$ SYSTEM (46)



or a change in silica content of 1.2 per cent in a slag weight of 5 gm. It was thus necessary to balance the forward and back reactions by approaching from about the same distance on either side of the equilibrium pressure. It is difficult to estimate exactly how closely this ideal was followed since the changes in volume during heating and sampling have to be taken into account, but it is considered that the net change in pressure during a run was never as high as 10 cm.

Some change in composition must also take place by diffusion of silicon monoxide vapour from the crucible. The weight of deposit on the tube after a run was about 0.02 - 0.03 gm., and some of this was probably due to reaction between the crucible and the mullite tube, so that the decrease in silica content due to this effect could not be greater than 0.5 per cent.

At first a gas sample was drawn after each reaction pressure determination, but as gas sampling introduces some uncertainty into the net pressure change and since the carbon monoxide contents were so uniformly high (always above 98 per cent) it was considered necessary to take only one gas sample during each run.

The general procedure used in the experiments on solid silica was followed in the slag runs. In general reaction velocities were greater, especially in the more fluid basic slags, and rather shorter runs were therefore possible than were considered advisable when all the constituents were solid.

(4) Results.

Some 20 runs were carried out in the earlier part of the work before the data on pure silica had been obtained. These runs gave results of the same order as those obtained in the later runs, but they did not show the same consistency, and have not been included here. The main reasons for the variations obtained are considered to be:-

(a) Great difficulty was being experienced with leaks in tubes and thermocouple sheaths, and many of the runs were invalidated for this reason.

(b) Adosrption effects made satisfactory degassing of the reaction chamber very difficult, and it was often difficult in consequence to decide whether or not leaks were present.

(c) Due partly to the use of impure carbon monoxide the gas was seldom of the purity which appears to be necessary in obtaining consistent results.

(d) In order to conserve tubes and thermocouple sheaths which were in very short supply, frequent adjustments of pressure were made so that the equilibrium pressure could be ascertained quickly. As a result some of the pressure changes observed may have been due to the "recovery" effect.

The results of all the runs done in the later stages of the work, after the pure silica runs had been completed, have been included, and are shown in Tables VIII - XIII. Some of the pressure/time curves from which the values of $p_{CO} + p_{SiO}$ have been obtained are shown in Figs.16, 17 and 18. These runs are typical of those carried out. As can be seen from them the greater reaction rates and higher gas purity in this series of runs have enabled equilibrium to be reached quite quickly from both above and below, especially in the more basic slags.

In cases where results have been duplicated by separate runs using fresh charges, this has been shown on the tables by separating the results by a line. Where no line is shown the results have been obtained with the same charge but with measurements at other temperatures intervening.

The activities obtained have been plotted against liquid composition in Figs.19 and 20. Comparison of the two curves shows that at silica contents below about 63 per cent, replacement of 20 per cent lime by 20 per cent alumina, has increased the silica activity, while above 63 per cent silica replacement of lime by alumina has decreased the silica activity. Since the slags used for the measurements on the binary system contained approximately 0.7 per cent alumina a slight correction must be applied to obtain the true binary curve. In view of the effect of alumina noted above it is apparent that the measured curve should be moved slightly to the right at low silica contents and slightly to the left at high silica contents.

The extent of the required shift is very small, but it has been indicated on Fig.19 for 1550°C at high silica contents where it can be fixed by the two silica saturation compositions.

The results show little temperature effect in the $CaO-SiO_2$ system, except at compositions nearing silica saturation. Unfortunately the steepness of the curve at this end has made some scatter of the experimental points inevitable, but the true activity lines can be drawn in with sufficient accuracy from the silica saturation compositions as read from Fig.14. At lower silica contents the line is well established, especially at 1550°C, which is the only temperature at which a continuous range of liquid compositions exists.

In the slags containing 20 per cent alumina there is a small decrease in activity with increasing temperature at the high-silica end, but this difference disappears at more basic compositions. Although no duplicates were carried out in this system, the variation in silica activity with temperature and composition is so consistent that the positions of the activity-composition lines appear to be well established.

TABLE VIII.

$CaO-SiO_2$ System 1450°C

No.	Analysis CaO	Analysis SiO_2	Analysis Al_2O_3	Measured $p_{CO}+p_{SiO}$	p_{SiO} (atm.)	p_{CO} (atm.)	a_{SiO_2}	N_{SiO_2} in Liquid.
C.S.3	51.3	47.7	0.79	0.308	0.010	0.298	0.635	0.611
C.S.4	42.0	57.5	0.60	0.312	0.010	0.302	0.652	0.611
C.S.5	41.4	58.8	0.7	0.354	0.011	0.343	0.844	0.611
C.S.5	41.4	58.8	0.7	0.367	0.011	0.356	0.907	0.611
C.S.6	34.3	66.0	0.80	0.373	0.012	0.361	0.932	0.631

TABLE IX.

$CaO-SiO_2$ System 1500°C.

No.	Analysis			Measured	p_{SiO} (atm).	p_{CO} (atm.)	a_{SiO}	N_{SiO_2} in Liquid.
	CaO	SiO_2	Al_2O_3	$p_{CO}+p_{SiO}$				
C.S.1	55.5	43.4	0.8	0.240	0.008	0.232	0.112	0.425
C.S.1	55.5	43.4	0.8	0.233	0.008	0.225	0.105	0.423
C.S.2	51.3	47.7	0.8	0.288	0.010	0.278	0.160	0.463
C.S.3	46.2	53.1	0.8	0.521	0.017	0.504	0.527	0.557
C.S.4	42.0	57.5	0.60	0.501	0.016	0.485	0.490	0.557
C.S.5	41.4	58.8	0.7	0.553	0.018	0.535	0.595	0.568
C.S.6	34.3	66.0	0.8	0.635	0.021	0.614	0.784	0.642
C.S.6	34.3	66.0	0.8	0.676	0.023	0.653	0.888	0.642

TABLE X.

$CaO-SiO_2$ System 1550°C.

No.	Analysis			Measured.				
	CaO	SiO_2	Al_2O_3	$P_{CO}+P_{SiO}$	P_{SiO} (atm.)	P_{CO} (atm.)	a_{SiO_2}	N_{SiO_2}
C.S.1	55.5	43.4	0.8	0.419	0.014	0.405	0.109	0.423
C.S.1	55.5	43.4	0.8	0.380	0.013	0.367	0.090	0.423
				0.408	0.014	0.394	0.103	0.423
C.S.2	51.3	47.7	0.7	0.584	0.020	0.564	0.210	0.463
C.S.3	46.2	53.1	0.6	0.735	0.025	0.710	0.334	0.516
C.S.4	42.0	57.5	0.6	Gas analysis only 91.6% CO				
C.S.5	41.4	58.8	0.7	0.903	0.031	0.872	0.578	0.569
C.S.6	34.3	66.0	0.8	1.152	0.039	1.113	0.808	0.643
C.S.6	34.3	66.0	0.8	1.158	0.039	1.119	0.831	0.643

TABLE XI.

$CaO-Al_2O_3-SiO_2$ System 1450°C.

No.	Analysis. CaO	SiO_2	Al_2O_3	Measured. $p_{CO} + p_{SiO}$	p_{SiO} (atm.)	p_{CO} (atm.)	a_{SiO_2}
CAS.1	46.7	33.5	20.25	0.082	0.003	0.079	0.045
				0.090	0.003	0.087	0.054
CAS.2	43.4	38.5	19.4	0.117	0.004	0.113	0.090
CAS.3	38.8	42.0	19.5	0.173	0.005	0.168	0.202
CAS.4	35.7	45.0	19.6	0.218	0.007	0.211	0.318
CAS.5	27.2	54.0	19.7	0.299	0.009	0.290	0.602
CAS.6	11.0	69.5	19.9	0.363	0.011	0.352	0.886

TABLE XII.

$CaO-Al_2O_3-SiO_2$ System 1500°C.

No.	Analysis.			Measured	p_{SiO}	p_{CO}	a_{SiO_2}
	CaO	SiO_2	Al_2O_3	$p_{CO}+p_{SiO}$	(Atm.)	(atm.)	
CAS.1	46.7	33.5	20.25	0.148	0.005	0.143	0.043
CAS.2	43.4	38.5	19.4	0.206	0.007	0.199	0.082
CAS.3	38.8	42.0	19.5	0.314	0.010	0.304	0.192
CAS.4	35.7	45.0	19.6	0.380	0.013	0.367	0.300
CAS.5	27.2	54.0	19.7	0.539	0.018	0.521	0.565
				0.532	0.018	0.514	0.550
CAS.6	11.0	69.5	19.9	0.656	0.022	0.634	0.836

TABLE XIII.

$CaO-Al_2O_3-SiO_2$ System 1550°C.

No.	Analysis. CaO	SiO_2	Al_2O_3	Measured. $p_{CO}+p_{SiO}$	p_{SiO} (atm.)	p_{CO} (atm.)	a_{SiO_2}
CAS.1	46.7	33.5	20.25	0.257	0.009	0.248	0.041
CAS.2	43.4	38.5	19.4	0.365	0.013	0.352	0.082
CAS.3	38.8	42.0	19.5	0.538	0.019	0.519	0.179
CAS.4	35.7	45.0	19.6	0.645	0.022	0.623	0.258
CAS.5	27.2	54.0	19.7	0.940	0.032	0.908	0.548
CAS.6	11.0	69.5	19.9	1.135	0.039	1.096	0.795

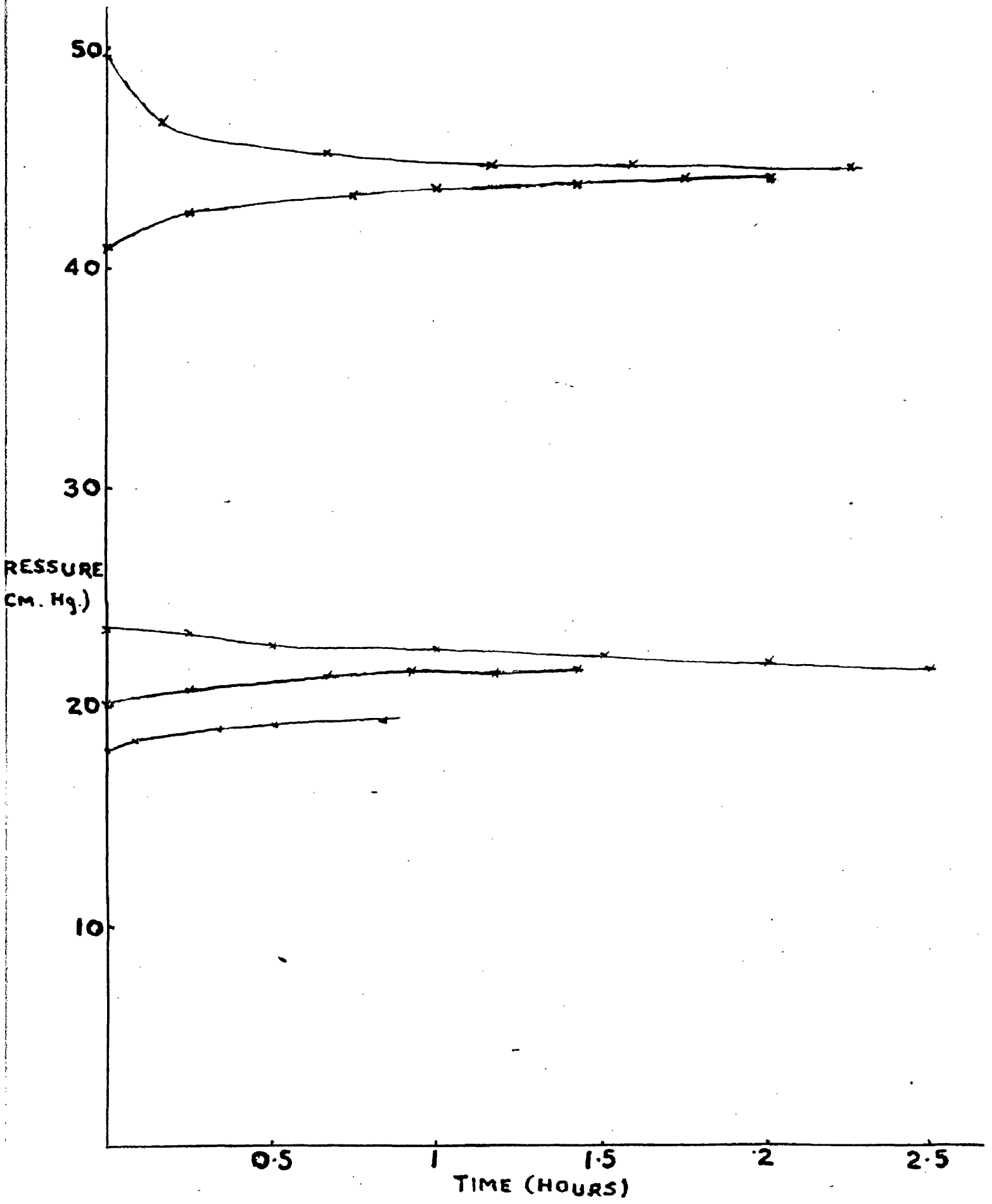


FIG. 16. PRESSURE/TIME CURVES FOR SLAG C.S.2

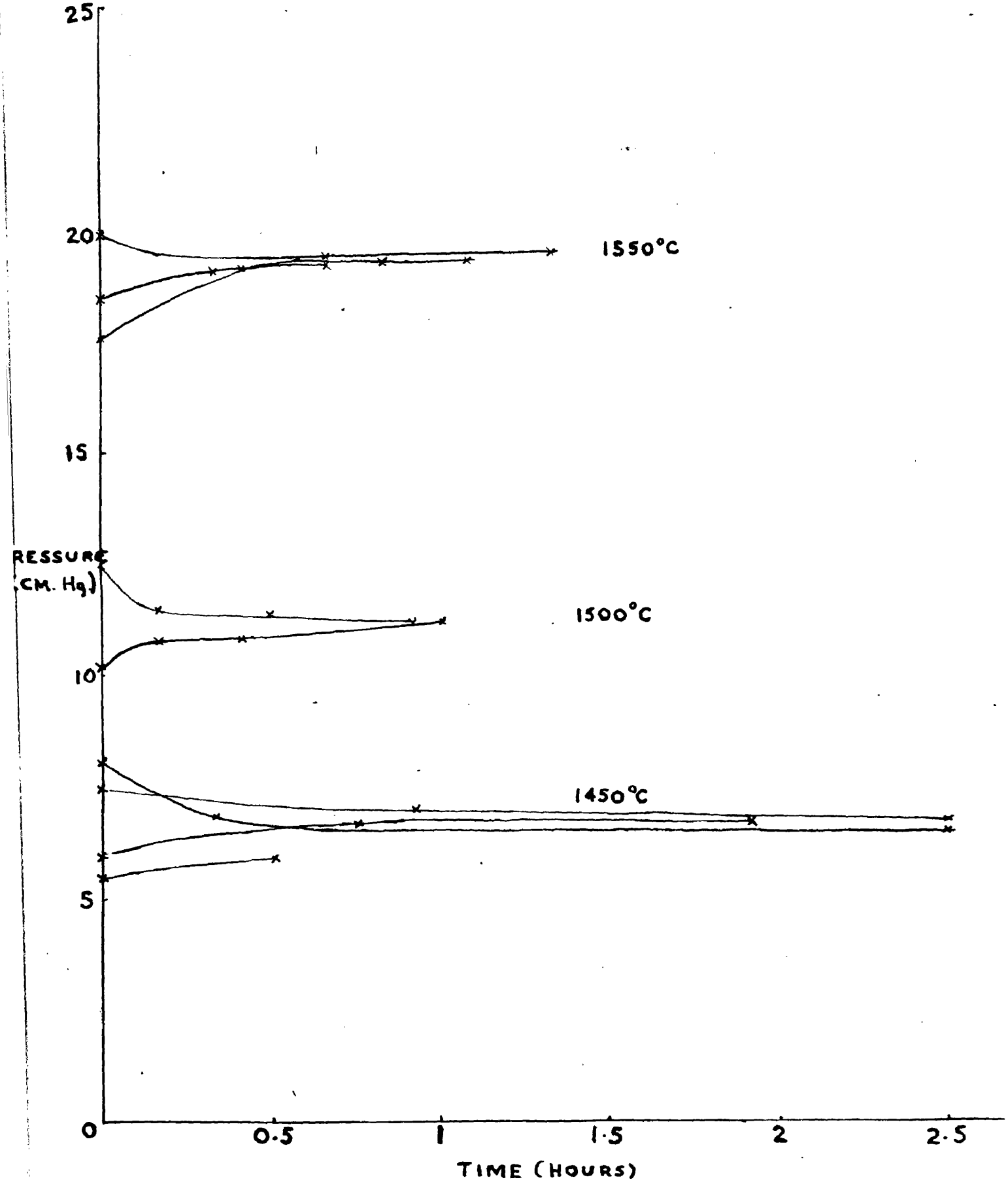


FIG. 17 . PRESSURE / TIME CURVES SLAG CAS. I .

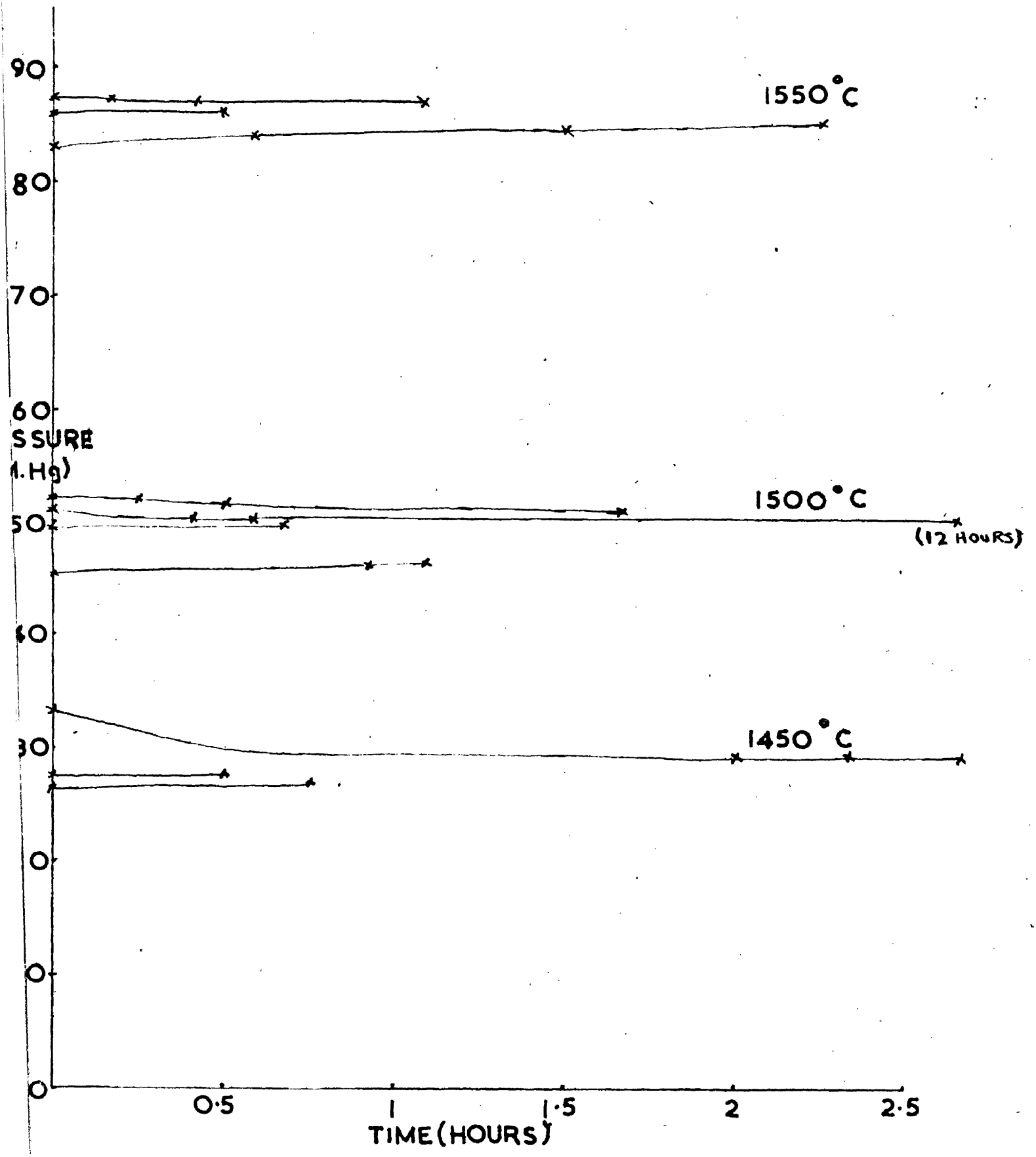


FIG.18 . PRESSURE / TIME CURVES FOR SLAG CAS.6 .

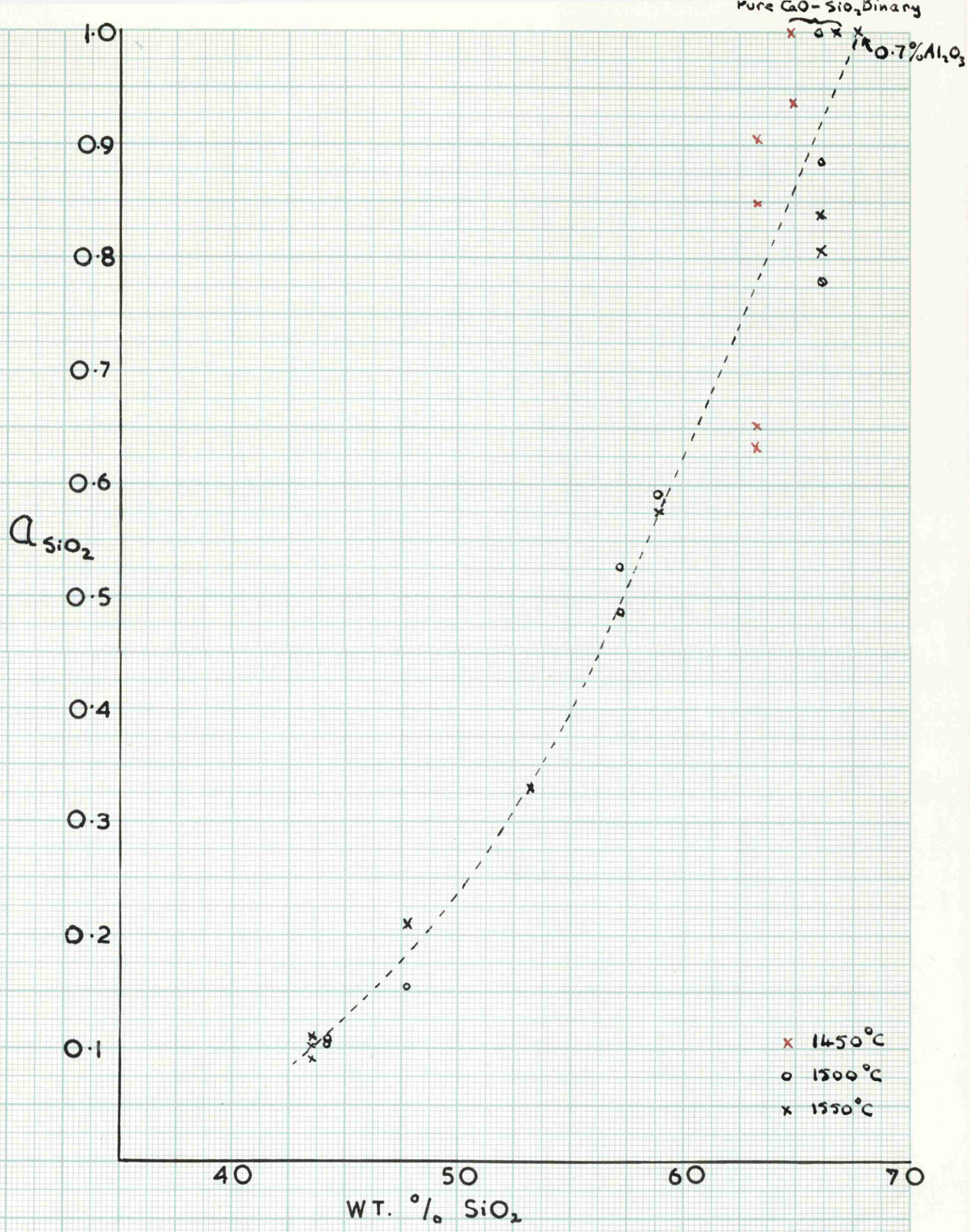


FIG. 19. ACTIVITY OF SiO_2 IN $CaO-SiO_2$ SLAGS

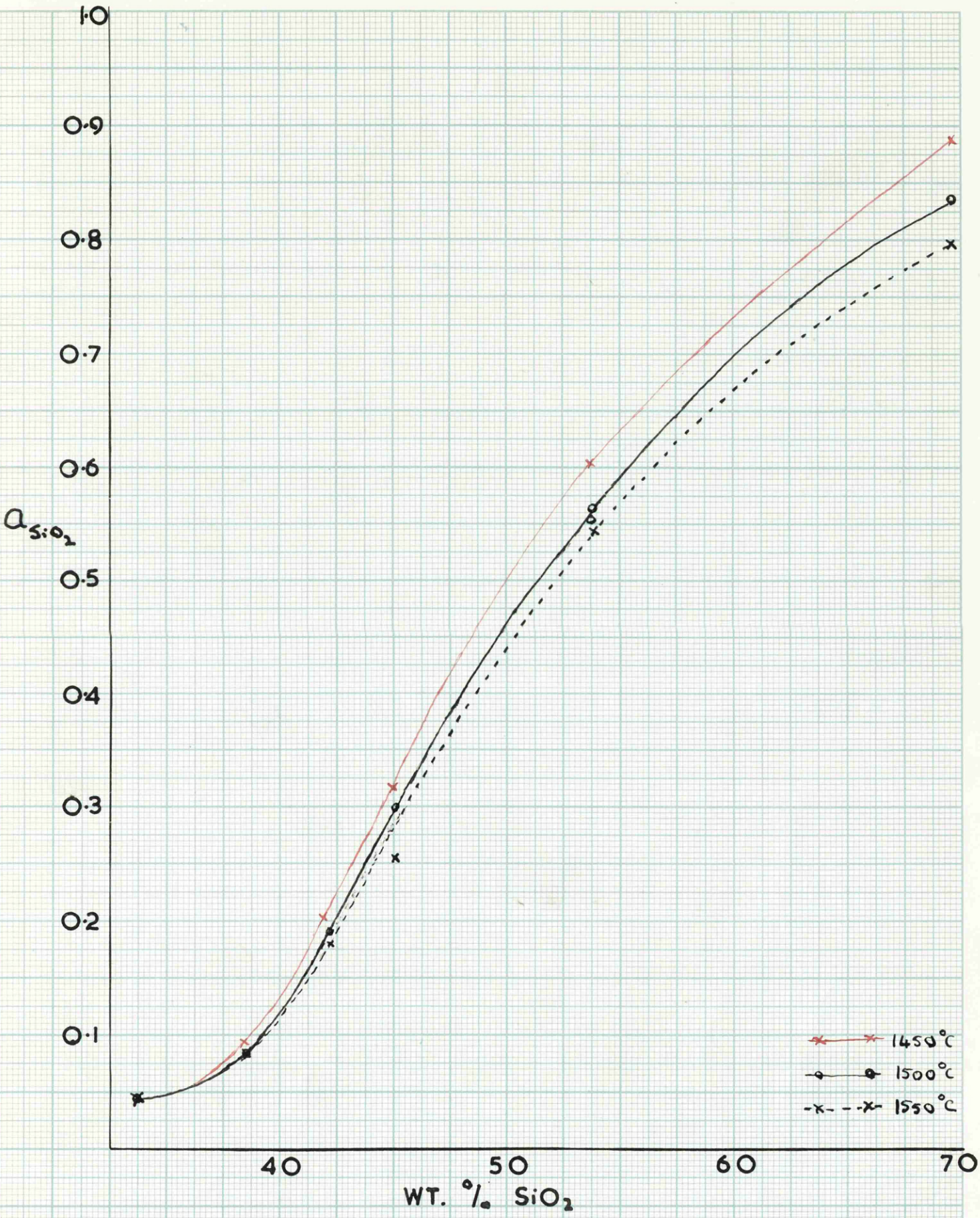


FIG. 20. ACTIVITY OF SiO_2 IN $CaO-SiO_2-20\%Al_2O_3$ SLAGS.

CHAPTER 6.

DISCUSSION OF RESULTS.

(1) The Si-C-O System.

Prior to the present work, the only direct measurements which have been made of reaction pressures in this system were by Brunner(43). The results obtained are shown graphically in Fig.21. The directions from which each point were approached have been indicated.

The single line obtained by the present experiments and the line calculated from existing data for the reaction $SiO_2 + 3C = SiC + 2CO$, have also been shown.

As can be seen from Fig.21, the methods used by Brunner to establish the phase-field boundaries were not very satisfactory. In the range below 1560°C the line for the reaction $SiO_2 + 3C = SiC + 2CO$, was established by the use of pellets containing only silica and carbon. It was thus possible to approach from the low-pressure side only, and the large volume of the reaction space used (6 litres) made the detection of small pressure changes difficult. Preheated silica and carbon pellets were used in order to obtain a series of pressures which were ascribed to the reaction between metastable siloxicon and silicon carbide. However, the preheated pellets would be expected to contain some silicon carbide, which would allow reaction to take place in the direction shown.

Brunner did not enclose his pellets in a crucible as he was unaware of the errors which might be introduced by the diffusion of silicon monoxide. In consequence his results may be affected in some of the ways outlined in Chapter 3. This is one possible explanation for the very low results obtained with mixtures containing silica, silicon carbide and carbon.

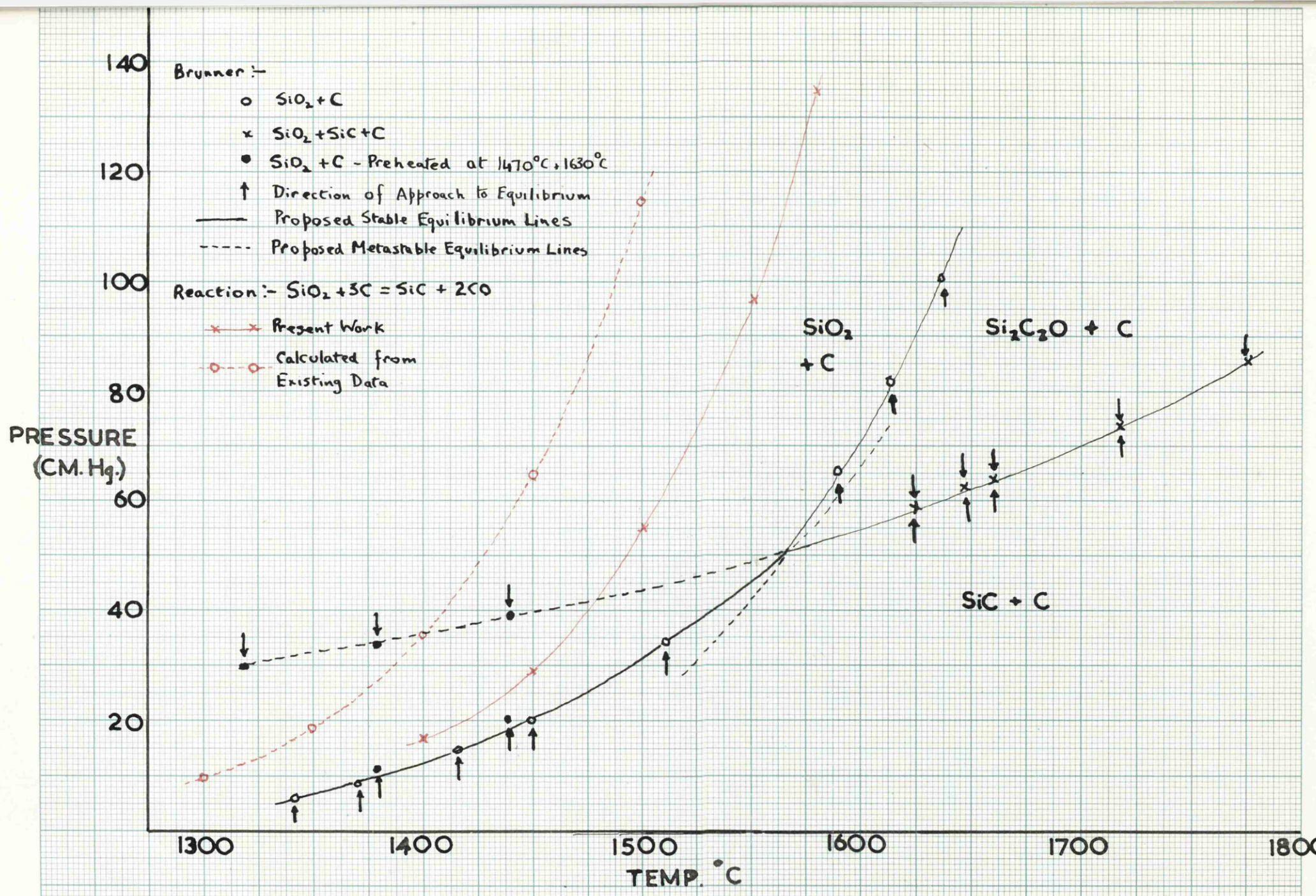


FIG. 21 REACTION PRESSURE MEASUREMENTS BY BRUNNER (43) ON Si-C-O SYSTEM

As was pointed out previously, there is no structural or analytical evidence for the existence of any ternary Si-C-O compound such as siloxicon (Si_2C_2O). Since the present experiments were carried out below 1580°C, the possibility that such a compound is stable above this temperature cannot be ruled out, but it may be noted that the evidence put forward for its existence by Brunner is not at all conclusive. It was based mainly on the fact that higher reaction pressures were obtained with silica-carbon mixtures than with silica-silicon carbide-carbon mixtures. As was shown in Chapter 3, this is to be expected from the effect of silicon monoxide diffusion.

Humphrey, Todd, Coughlin and King(25) commented on Brunner's reaction pressure determinations and suggested that they conformed to the equilibria:-

$$SiO_2 + C = SiO(g) + CO \quad \text{.....(1)}$$

$$\text{and } 2SiO(g) = Si + SiO_2 \quad \text{.....(2)}$$

since the equilibrium value of p_{SiO} for reaction (2) would control the value of p_{CO} for reaction (1) to approximately that measured by Brunner. However, reactions (1) and (2) are equivalent to the single equilibrium:-

$$SiO_2 + 2C = Si + 2CO \quad \text{.....(3)}$$

There seems to be no reason why metallic silicon should be stable in the presence of carbon, and reaction between carbon and silicon would re-establish the equilibrium:-

$$SiO_2 + 3C = SiC + 2CO \quad \text{.....(4)}$$

As can be seen from Fig.21, the reaction pressures measured in the present work are only about half those obtained by calculation from the previously available thermodynamic data. The reasons for deciding that the measured pressures are the true equilibrium pressures for the reaction:

$$SiO_2 + 3C = SiC + 2CO \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

were advanced in Chapter 4, but additional evidence for this conclusion may be noted here. It was shown in Chapter 3 that an error in the measured pressure might be possible if there was a wide difference in the rates of the two reactions:-

$$SiO_2 + C = SiO(g) + CO \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

and

$$SiC + CO = SiO(g) + 2C \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The solution of silica in a slag would be expected to increase the reaction rate of (1) and leave (5) unchanged, but the measured carbon monoxide pressures for silica saturated slags were if anything slightly lower than those obtained with pure silica.

It thus appears impossible that the large difference between the observed and calculated pressures can be attributed to silicon monoxide diffusion.

Since the free energies of formation of carbon monoxide and silica have been established by a number of workers, and since the entropy of silicon carbide also appears to be reliably checked, the discrepancy in the thermodynamic data must be in the heat of formation of silicon carbide, as determined by Humphrey, Todd, Coughlin and King(25). The values which they obtained were:

$$Si(c) + C = SiC \text{ (hexagonal, mod.II)}$$

$$\Delta H^{\circ}_{298.16^{\circ}K} = -12{,}310 \pm 920 \text{ cal.}$$

$$Si(c) + C = SiC \text{ (cubic)}$$

$$\Delta H^{\circ}_{298.16^{\circ}K} = -13{,}400 \pm 920 \text{ cal.}$$

Values of $\Delta_f H^{\circ}_{298.16^{\circ}K}$ in the region of - 8,000 cal., would be required to agree with the present data.

No source of such a large error is evident from an examination of the experimental technique used by Humphrey et. al. The determination of the heat of combustion of silicon carbide was carried out by burning a mixture of silicon carbide and titanium powder in oxygen at 40 atmospheres pressure, the powder being contained in a rutile-lined capsuls. Corrections were applied for incomplete combustion of titanium to rutile (TiO_2) and for a difference in heat of formation of a deposit, amounting to 11 per cent by weight of the combustion product, which was formed on the walls of the bomb. The methods used for these corrections appear somewhat arbitrary, but errors due to these factors alone could not produce the required difference.

It must be noted, however, that the value of the heat of combustion is nearly 300,000 cal/mole and that the measured heat evolution correspond to a much higher value than this due to the combustion of titanium powder, so that an error of 4,500 cal/mole in $\Delta H^{\circ}_{298^{\circ}K}$ represents a very small fraction of the total heat evolved per mole of silicon carbide. In consequence an error of this magnitude is not impossible, and indeed previous determinations have shown even greater discrepancies For example Ruff and Grieger's measurements gave a value of $\Delta H^{\circ}_{298^{\circ}K}$ of -26,700 cal./mole.

Fulton and Chipman(21) cited the work of Taylor and Laidler(47) in support of their belief that silica, silicon carbide and 1 atmosphere pressure of carbon monoxide were in equilibrium with each other at 1456°C (as predicted from previous thermodynamic data). Taylor and Laidler had found that silicon carbide was only formed from silica and carbon at temperatures above about 1450°C, but examination of the experiments in question shows that they were carried out in vacuum and not at 1 atmosphere pressure of carbon monoxide, as assumed by Fulton, and Chipman. The present work shows that the four phases in their standard states are in equilibrium at 1560°C.

The free energy of formation of silicon carbide is of great importance in the chemistry of iron-carbon-silicon alloys and hence of Fe-Si alloys. The compositions of the Fe-Si-C alloys in equilibrium with silicon carbide and carbon may be easily determined at different temperatures, and if the free energy of formation of silicon carbide is known, the activities of silicon in these alloys can be calculated. Chipman, Fulton, Gokcen and Caskie(22) measured the activity of silicon in Fe-Si and Fe-C-Si alloys independently of this method, and over a wide range of compositions by finding the distribution of silicon between these alloys and immiscible silver-silicon alloys. The silicon activity measured by this method at the composition in equilibrium with silicon carbide and carbon agreed very well with the value calculated from the data of Humphrey et al(25), on the free energy of silicon carbide. Due to this close agreement, the silicon activities measured by the

silver distribution method appeared until now to be well established. The value of ΔG°_{SiC} now obtained shows that, at high silicon contents, the silicon activities in Fe-Si-C alloys (and correspondingly in Fe-Si alloys) must be higher than had formerly been considered.

The effects of the new silicon carbide data in this field will be discussed more fully in Part II.

(2) The Activity of Silica in Slags.

(a) Lime-Silica Slags. In Fig.22, the plot of a_{SiO_2} against N_{SiO_2} obtained at 1550°C from the present work has been shown, together with the results of other workers. The standard state of silica for all these curves is β- cristobalite.

In comparing the present results with those of other workers, it is useful to try to estimate the probable accuracy of the activity values obtained. This is difficult, for although the method is direct and does not rest on any assumptions, the accuracy depends on several factors which vary from one measurement to another. These are:-

(i) Temperature - within the limits of the apparatus, higher temperatures give higher accuracy by increasing reaction rates and pressures.

(ii) Slag viscosity - more fluid slags give greater reaction rates.

(iii) Silica activities - high reaction pressures, which are associated with high silica activities, can be measured

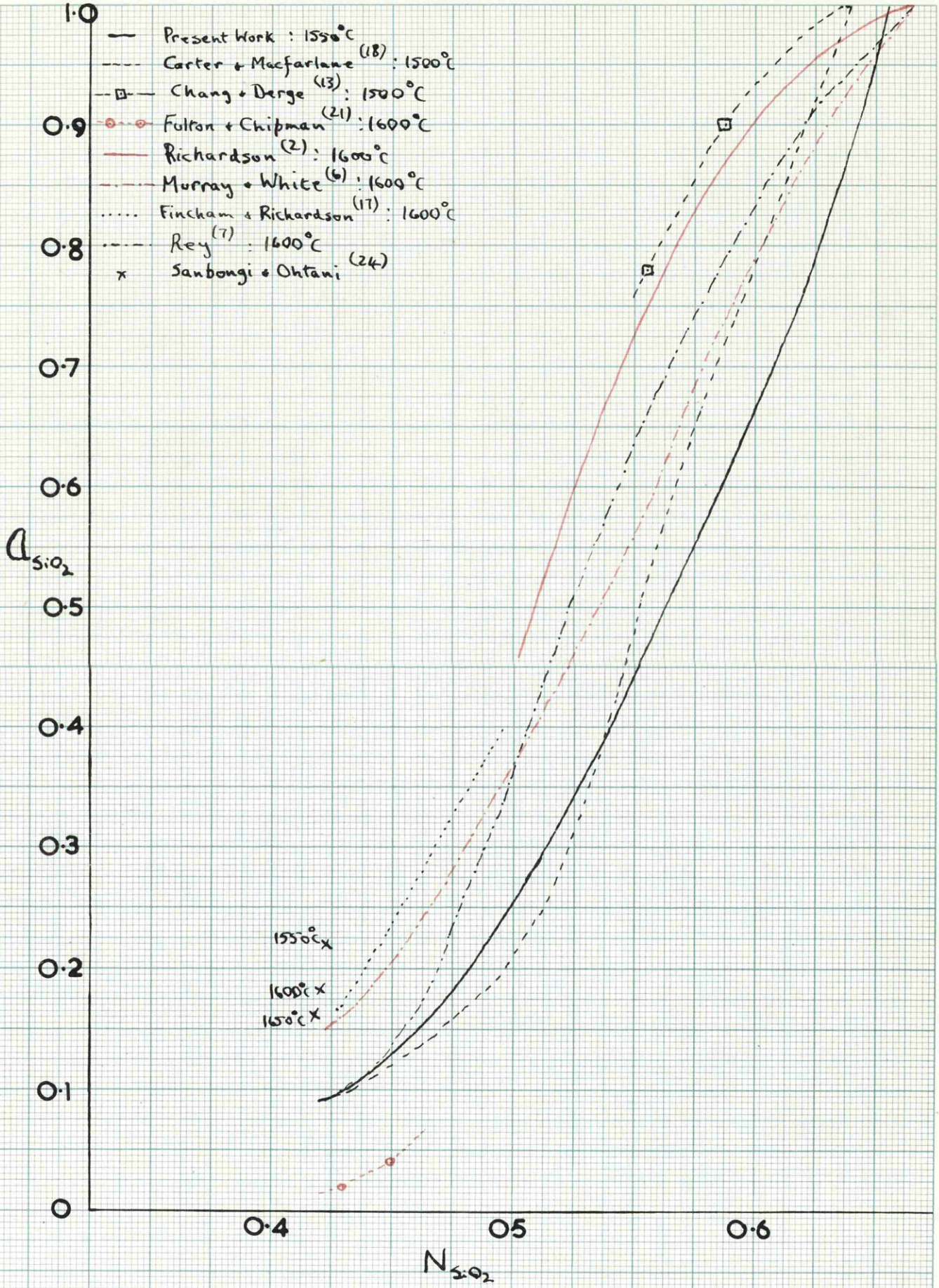


FIG. 22. ACTIVITY OF SiO_2 IN $CaO-SiO_2$ SLAGS

with greater accuracy than low pressures, providing that the temperature control is made sufficiently accurate.

(iv) Slag composition - the fixing of the slag composition, both by analysis and by controlled approach to equilibrium, is of great importance in determining the accuracy where the activity-composition curve rises steeply.

Considering the scatter in duplicate results at the lime-rich end of the binary system at 1550°C *, individual activity measurements are considered to be accurate to within ± 10 per cent in this region At higher silica contents the experimental error may be somewhat greater, since the effect of greater reaction pressures is probably more than offset by the difficulty of fixing the slag composition exactly and by the decreased reaction rates. In addition to the experimental errors, there may be a small systematic error due to an error in the measurement of the equilibrium constant for the reaction. Although this would increase the error in an individual measurement slightly, the smooth curve drawn through the mean of the experimental points at 1550°C is still considered to be correct to within ± 10 per cent.

It can be seen from Fig.22 that the results of Fulton and Chipman (21) are below those of all other workers, and are well beyond the proposed accuracy limits for the present work. As was indicated in Chapter 2, the probable reason for the lowness of these results, which were obtained by slag-metal equilibrium measurements, is that the silicon activity values used by Fulton and Chipman for the calculation

* For slag CS.1 the results obtained were 0.109, 0.090 and 0.103 at 1550°C and 0.105 and 0.112 at 1500°C.

of silica activities were too low. Arthur(23) has shown that the extrapolation of Chipman, Fulton, Gokcen and Caskie's(22) results to higher carbon contents was not valid, but the new silicon carbide free energy indicates that the experimental results obtained by the silver distribution method are also in error over a fairly wide range of composition. Fulton and Chipman's values of a_{SiO_2} are of the same order as would be obtained from the present results if they were calculated on the basis of the silicon carbide free energy data of Humphrey et al.(25).

Fulton and Chipman's values of a_{SiO_2} in the $CaO-SiO_2$ system had formerly received support from Richardson's(2) curve, which was calculated from the free energy data on the calcium silicates assembled by Richardson, Jeffes and Withers(48). However, Fincham and Richardson(17) have now withdrawn the portion of this curve below $N_{SiO_2} = 0.5$ in the light of their measurements on the sulphide capacities of $CaO-SiO_2$ slags. The curve based on the latter work can be seen from Fig.22 to be considerably higher than that indicated by the present work, as is the portion of Richardson's(2) original curve above $N_{SiO_2} = 0.5$.

As shown in Fig.22, much better agreement exists between the present activity values and those of Carter and Macfarlane(18). The latter were calculated from lime activities by the Gibbs-Duhem relation, the lime activities being obtained from slag-gas equilibrium measurements on the reaction:-

$$(CaO) + \tfrac{1}{2}S_2 = (CaS) + \tfrac{1}{2}O_2 \quad \ldots\ldots\ldots\ldots(6)$$

In order to calculate the activity of lime from the experimental results, a knowledge of the activity of calcium sulphide was necessary, and the

assumption was used that the variation of a_{CaS} with % CaS would be similar for all the slags used, following Henry's Law in dilute solution but exhibiting negative deviation from Henry's Law as saturation is approached. The close agreement of the silica activity curve thus obtained with the present one lends support to the validity of this assumption.

Comparison of Carter and Macfarlane's work with that of Fincham and Richardson(17), in which a very similar experimental technique was used, is made difficult by the fact that the latter workers assumed a value of 5 for % CaS whereas Carter and Macfarlane used values of % CaS of about 12. Different free energy data were also used for the calculation of the sulphurising potential of the gas mixtures. Experimentally the two sets of data agree fairly closely, but Carter and Macfarlane(18) appear to have covered the composition range from N_{SiO_2} = 0.42 to N_{SiO_2} = 0.5 more fully than did Fincham and Richardson (17).

It is difficult to assess the probable accuracy of Chang and Derge's(13) silica activities, which were determined by electro-motive-force measurements. The experimental difficulties of this method were found to be considerable, and it was impossible to establish the cell reaction with any degree of certainty. In addition the iso-activity lines which they obtained in the $CaO-Al_2O_3-SiO_2$ system do not conform to the direction expected from the slope of the silica saturation curve, and although this anomaly may only be connected with the presence of alumina in the slag, little reliance can be placed on this

method until the reason for it is known. The values obtained by them in the $CaO-SiO_2$ binary are shown in Fig.22, and can be seen to be considerably higher than these indicated by the present work.

Sanbongi and Ohtani(24) measured the silica activities of $CaO-SiO_2$ slags saturated with Ca_2SiO_4 at 1550, 1600 and 1650°C. The three results obtained have been plotted on Fig.19. The reaction used for the measurements was:-

$$(SiO_2) + 2H_2 = \underline{Si} + 2H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Values of a_{Si} in Fe-Si alloys were first determined by using pure silica in this reaction, and measuring the silicon content of the metal for different p_{H_2}/p_{H_2O} ratios. The values of a_{Si} found in this way were then used to interpret the results obtained using a lime-silica slag instead of pure silica. However, in more recent papers(49),(50), the authors have obtained different values of a_{Si} in Fe-Si alloys by E.M.F. measurements, so that great reliance cannot be placed on their values of a_{SiO_2}.

In lime-rich slags agreement of the present curve with the estimated curve of Rey(7) is good, but at higher silica contents the two curves diverge considerably. Murray and White's(6) calculated curve shows slightly higher silica activities than the present work throughout almost the whole range of compositions. However, in view of the semi-empirical nature of both these methods of estimating silica activities, more exact agreement could not be expected than that obtained with Murray and White's curve.

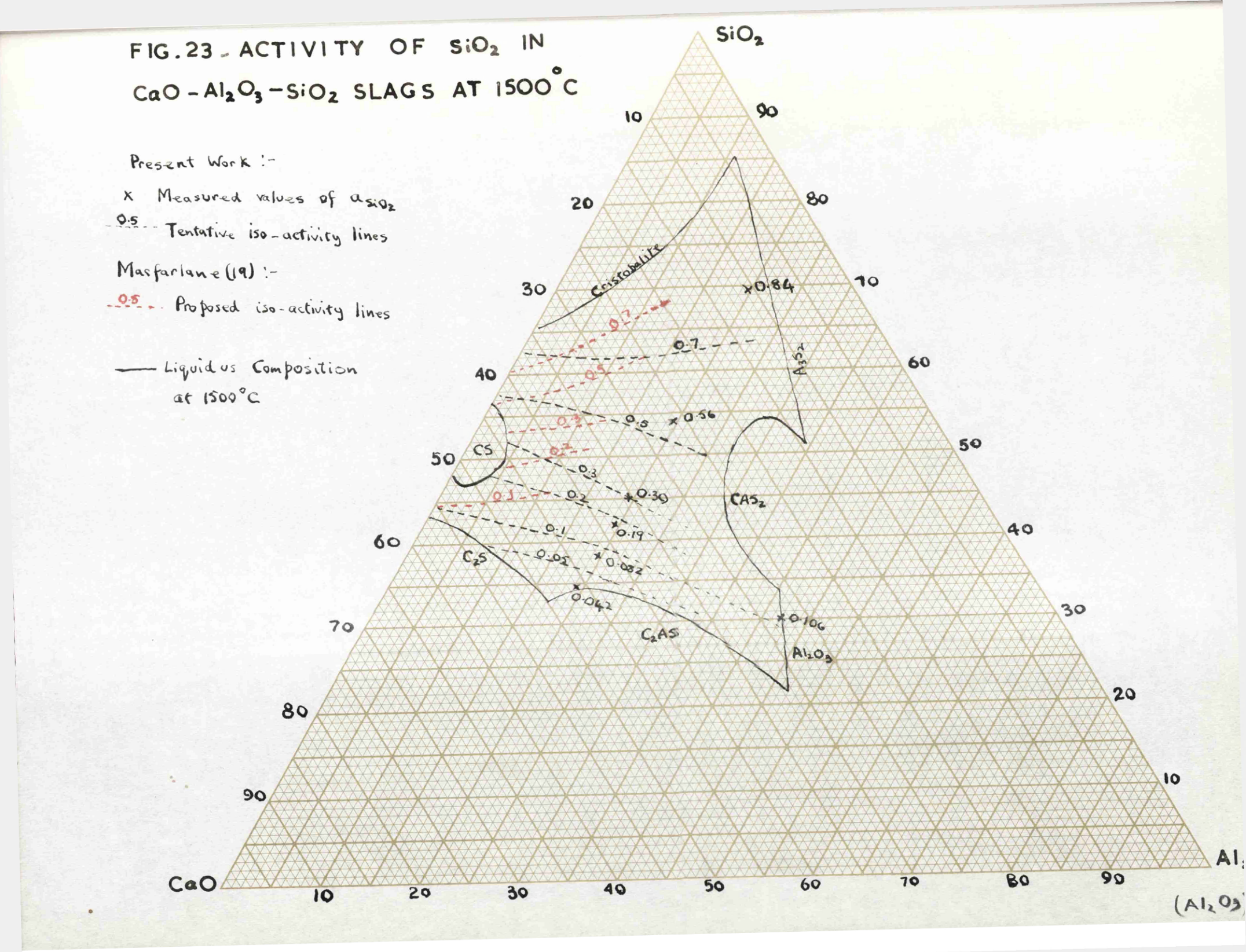
Summarising the comparison of the data shown in Fig.22, it can be seen that the silica activity values obtained by the present method are in good agreement with the most recent experimental results of Carter and Macfarlane(18). Fincham and Richardson's(17) curve is somewhat higher than the present results, but Fulton and Chipman's(21) values are very much lower than them, and are also much lower than all the estimated silica activity curves. The fact that the present results, calculated on the basis of the new silicon carbide data, are of the same order as those of all other workers except Fulton and Chipman, lends support to the new free energy data for silicon carbide.

The agreement of the present work with that of Carter and Macfarlane(18) means that the present work would lead to the same values for the free energies of mono- and dicalcium silicates and for the free energy curve for lime-silica melts as were calculated by these workers.

(b) Lime-Alumina-Silica Slags. The silica activities measured in the six slags containing 20 per cent alumina at 1500°C are shown in Fig.23, and tentative iso-activity lines have been drawn in from these results together with those obtained in the binary system. The approximate position of the lines is fairly well established but values at 10 and 30 per cent alumina would be required to decide the curvature of the iso-activity lines accurately. *

* One additional result was obtained for the purposes described in Part II, and it was found that a slag containing 28 per cent SiO_2, 30 per cent CaO and 42 per cent Al_2O_3 had a silica activity of 0.106 at 1500°C. This result has been shown in Fig.23, and has allowed further extrapolation of the iso-activity curves in this region.

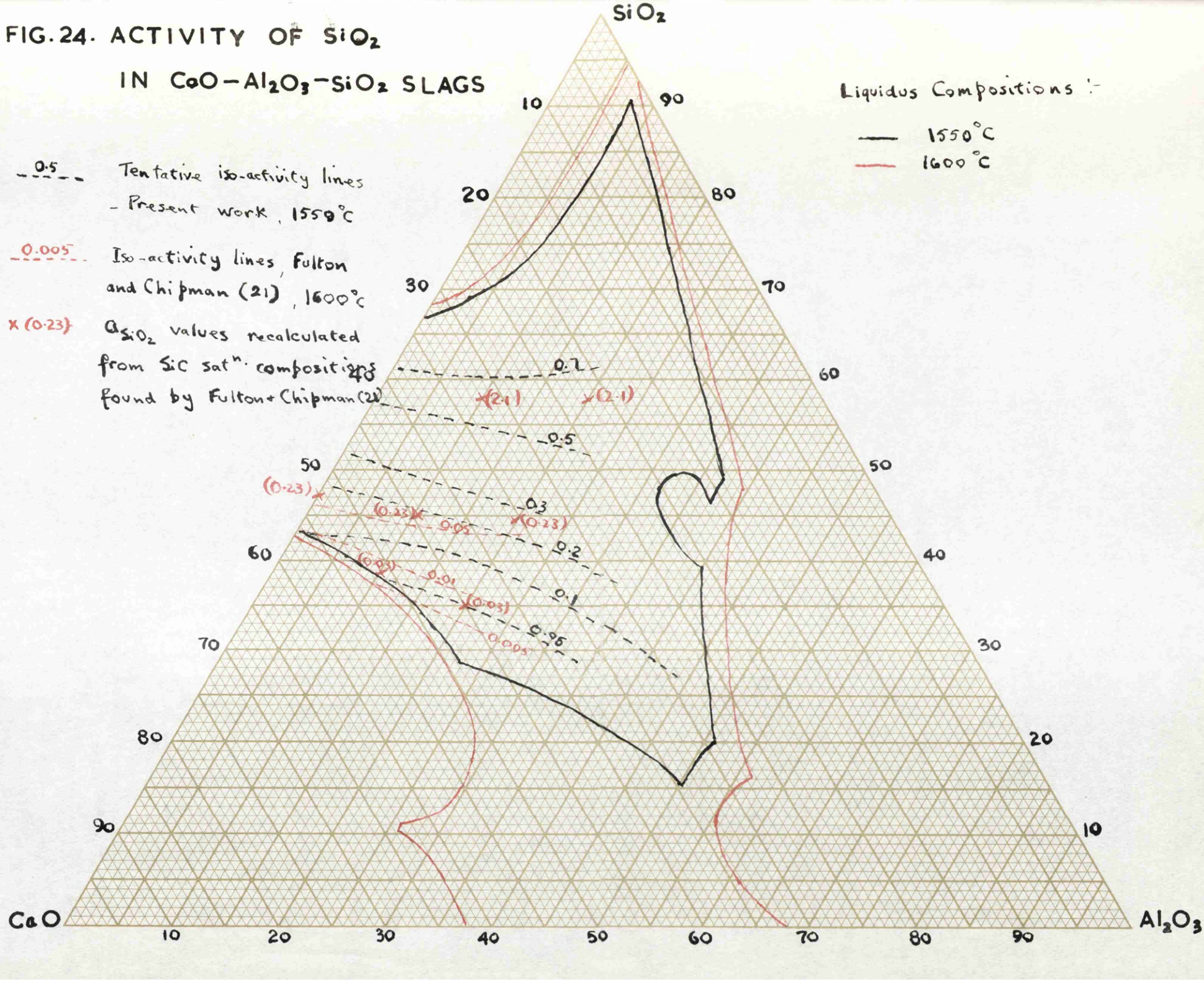
FIG. 23 - ACTIVITY OF SiO_2 IN $CaO - Al_2O_3 - SiO_2$ SLAGS AT 1500°C



Approximate silica activities calculated by Macfarlane(19) from measurements of the sulphur capacities of $CaO-Al_2O_3-SiO_2$ slags are also shown on Fig.23. The curves obtained by the latter method can be seen to slope upwards more quickly than those indicated by the present work. In view of the excellent agreement between the two methods in the binary system, and the fact that no additional assumptions were necessary in the measurement of a_{CaO} in the ternary system, it would seem probable that the discrepancy between the two sets of data arises from the method of calculating a_{SiO_2} from a_{CaO} in the ternary system. This was done by assuming that the activity of alumina would be constant along lines of constant $N_{Al_2O_3}$, and then using the Gibbs-Duhem equation to calculate silica activities from lime activities along these lines. As pointed out by Macfarlane the assumption made is unlikely to be strictly correct due to the fact that silica has a greater affinity for lime than has lime for alumina. This approximate method of calculating a_{SiO_2} in the ternary system, therefore, yields minimum values. The present work does, in fact, indicate higher values of a_{SiO_2} in the ternary system and can, therefore, be taken as giving the more reliable of the two sets of data without invalidating the values of a_{CaO} obtained by Macfarlane(19).

Although it is considered that the values of a_{Si} used by Fulton and Chipman(21) are in error, the directions of their iso-silica activity curves in the ternary system, being merely curves of constant silicon content in the metal, should be reliable. Fulton and Chipman's

FIG. 24. ACTIVITY OF SiO_2 IN $CoO-Al_2O_3-SiO_2$ SLAGS



equilibrium exists for the two slag compositions marked in Fig.24. The calculated values of $a_{SiO_2} = \frac{1}{K_4}$ at 1600°C and 1700°C are 0.23 and 0.03 respectively, and the corresponding slag compositions found by Fulton and Chipman are also shown in Fig.24. In contrast to the 1500°C results, the values of a_{SiO_2} obtained at 1600°C and 1700°C can be seen to be in excellent agreement with the present work.

In view of the fact that silica activities in the $CaO-SiO_2$ system are now fairly well established as being much higher than Fulton and Chipman's values, and that the directions of the iso-activity lines are well fixed, there is good support for the present values of a_{SiO_2} in the ternary system. Unless there is a very large temperature gradient in silica activities, the fact that Fulton and Chipman's equilibrium measurements at 1600°C and 1700°C agree so well with the present silica activity values mean that their measurements at 1500°C must be wrong. This follows because if the free energy of formation of silicon carbide is altered to give reasonable silica activities at 1500°C, then the silica activities measured at 1600°C and 1700°C would be made much lower than appears to be possible.

Although Fulton and Chipman's measurements at 1600°C and 1700°C would be expected to be more accurate than those made at 1500°C due to the higher reaction rates, such a large discrepancy between them is unexpected. However, it can be seen from Fulton and Chipman's curves showing the silicon content of the metal plotted against the silica content of the slag at 1500°C, that these curves do not establish saturation with silicon carbide at all conclusively. Saturation with

silicon carbide occurs when the silicon content of the metal reaches about 23 per cent, but the composition of the slag in equilibrium with this metal composition has been obtained by considerable extrapolation of a curve which is poorly defined by the experimental points. Since the two lines approach each other at an acute angle, a slight error in extrapolation may lead to quite a large error in fixing the point at which they meet. It is now considered that the two lines do not meet, and hence that at 1500°C there is no slag in equilibrium with a carbon-saturated Fe-Si-C alloy containing 23 per cent silicon when the carbon monoxide pressure is 1 atmosphere.

In contrast to the results at 1500°C, the curves at 1600°C and 1700°C do establish the slag compositions in equilibrium with silicon carbide quite accurately. The lines are well defined by the experimental points, and they approach the silicon carbide saturation composition at a wide angle, so that there is a much smaller margin of error in fixing the corresponding slag compositions.

The agreement between the slag activities calculated in this way at 1600°C and 1700°C with the results of the present work, means that Fulton and Chipman have established the same equilibrium as was used in the present work, by using an open crucible. This is added proof that the present results have not been affected by silicon monoxide diffusion.

As was shown by the present work reaction rates are much lower with viscous slags near silica saturation than with more basic slags, and this has probably prevented Fulton and Chipman from noticing the discrepancy in the silicon carbide free energy data, which should have

been apparent from their experiments at 1500°C. The present method of using changes in carbon monoxide pressure to establish the equilibrium is much more sensitive than Fulton and Chipman's method, in which changes in the silica content of the slag and the silicon content of the metal had to be followed to establish the equilibrium conditions.

It can thus be seen that the present results are in good agreement with the values indicated by the previous experimental data, including the most accurate measurements of Fulton and Chipman at 1600°C and 1700°C. Qualitatively it has been found (as can be seen by comparing Figs.19 and 20) that at silica contents above 65 per cent replacement of lime by alumina on a weight for weight basis decreases the silica activity, while below 65 per cent silica the reverse is true. In slags containing 20 per cent alumina, silica activities were found to decrease with increasing temperature where the silica content was above 40 per cent. Below this silica content no change with temperature was apparent.

PART II.

THE ACTIVITY OF SILICON IN IRON-CARBON-SILICON ALLOYS AND THE REACTION $(SiO_2)+2C = \underline{Si}+2CO$.

INTRODUCTION.

It was shown in Part I that it would be possible to calculate silica activities in $CaO-Al_2O_3-SiO_2$ slags from the slag-metal equilibrium data of Fulton and Chipman(21) if the activity of silicon in carbon saturated iron-carbon-silicon alloys were known. The work of Arthur(23) had appeared to show that the extrapolation made by Fulton and Chipman of the data of Fulton, Chipman, Gokcen and Caskey(22) on the activity of silicon in Fe-Si-C alloys was inaccurate, and would lead to silicon activities in carbon-saturated alloys which were too low.

Since the data obtained by Arthur(23) were insufficiently complete to allow the necessary silicon activities to be calculated accurately it was decided to attempt to measure the activity of silicon in these alloys by an independent method. This was intended to provide an alternative approach to the measurement of silica activities in slag.

Both the iron-carbon and iron-silicon binary systems exhibit strong negative deviations from ideality due to the strong attractive forces between Fe-C and Fe-Si atoms. The effect of the addition of carbon to an Fe-Si alloy is to raise the activity of silicon, probably due to the competition between silicon and carbon atoms for positions of low energy in the lattice. The effect of carbon on the activity coefficient of silicon may be expressed either by an interaction coefficient γ^{C}_{Si}, or by the use of an equivalent mole fraction N^{C}_{Si}. The value of γ^{C}_{Si} is obtained from the relationship:-

$$\gamma_{Si} = \gamma^{C}_{Si} \times \gamma^{Si}_{Si}$$

where γ_{Si} is the activity coefficient of silicon in the ternary solution,

and γ^{Si}_{Si} is the activity coefficient of the same mole fraction of silicon in the binary Fe-Si system.

In the alternative treatment, which is that used in the present work, the silicon equivalent of carbon, N^{C}_{Si} is defined by the equation:

$$N^{1}_{Si} = N_{Si} + N^{C}_{Si}$$

where N_{Si} is the mole fraction of silicon in the ternary alloy

and N^{1}_{Si} is the mole fraction of silicon in the binary Fe-Si system having the same value of activity coefficient, γ_{Si}, as the ternary alloy.

To make use of either of these convenient methods, an accurate knowledge of the activity of silicon in the iron-silicon binary system is necessary.

The data on the iron-silicon system which appeared most reliable were those of Chipman, Fulton, Gokcen and Caskey(22). These data were obtained by measuring the distribution of silicon between immiscible Ag-Si and Fe-Si alloys, the activity of silicon in both phases being equal at equilibrium. It was possible to estimate the activity of silicon in the Ag-Si alloys over the necessary range, and a check on the activity of silicon at high values of N_{Si} in the Fe-Si system could

be obtained by calculation from the Fe-Si phase diagram. The values of α_{Si} obtained by both methods were in quite good agreement, and the curve also appeared to be confirmed by data on the equilibrium of silicon carbide with carbon-saturated Fe-Si-C alloys. In their work on Fe-Si-C alloys, using the silver distribution method, Chipman, Fulton, Gokcen and Caskey had found that silicon and carbon were equivalent on a mole fraction basis, that is $N_{Si}^{C} = N_C$. On this basis both binary and ternary alloys should be represented by a single line in a plot of the activity coefficient of silicon against $N_C + N_{Si}$. In the course of the experiments described in Part I it became clear that the free energy equation for silicon carbide derived from the data of Humphrey, Todd, Coughlin and King(25) (which were used by Chipman et al(22)) was in error by quite a large amount. The effect of the change from this latter free energy equation to the one derived in Part I is shown in Fig.25, where $\log_{10} \gamma_{Si}$ has been plotted against $N_C + N_{Si}$. Whereas the former silicon carbide data had given a point almost exactly on the independently determined binary activity coefficient curve, the new data give a very much higher activity coefficient at the same composition. Since the alloy in equilibrium with carbon and silicon carbide at 1420°C contains only about 0.3% carbon, the correction for the effect of carbon on the activity coefficient of silicon is very small for this alloy. Consequently the silicon carbide saturation point virtually fixes a point on the activity coefficient curve for the Fe-Si system, so that the binary curve obtained by Chipman, Fulton, Gokcen and Caskey(22) at this

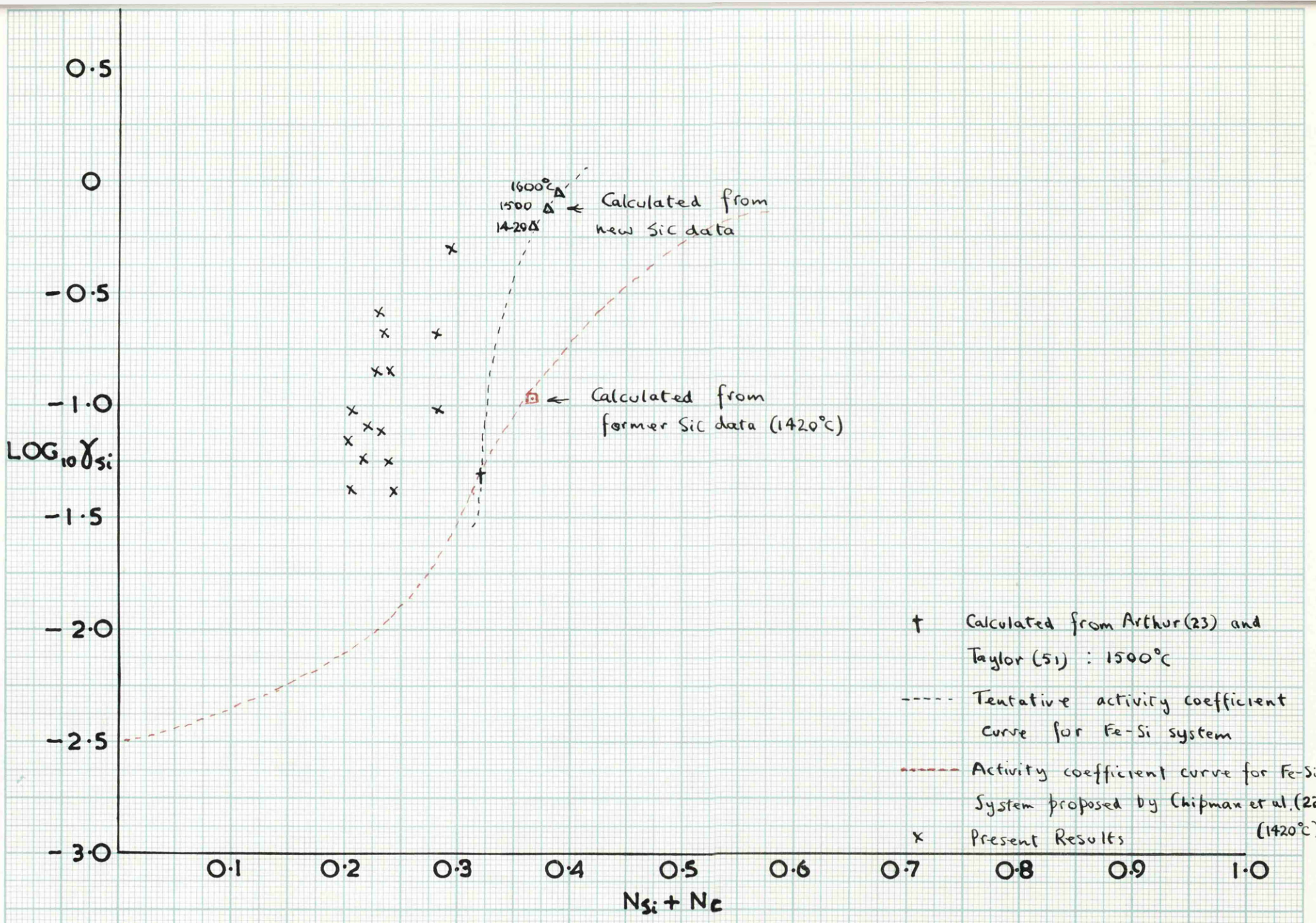


FIG. 25. ACTIVITY COEFFICIENT OF SILICON IN Fe–Si AND Fe–Si–C ALLOYS

point must be considerably in error.

As it is impossible to determine accurately the effect of carbon on the activity coefficient of silicon without accurate data on the activity of silicon in Fe-Si alloys, the present experimental work was discontinued as a method of making use of slag-metal equilibrium data to calculate silica activities in slags. However, since some degree of success was obtained with the experimental method of measuring silicon activities before it was discontinued, and since it is possible to use the slag activities obtained in Part I to obtain some silicon activities by the reverse calculation, it has been possible to draw tentative conclusions as to the shape of the activity coefficient curve for silicon in Fe-Si alloys and to estimate the approximate effect of carbon on that coefficient.

(2) EXPERIMENTAL MEASUREMENT OF SILICON ACTIVITIES.

The method used for the measurement of silicon activities in carbon saturated iron-silicon-carbon alloys was somewhat similar in principle to that used in Part I to measure silica activities in slags. In this case equilibrium was established between silicon dissolved in the metal, carbon, silica and a measured pressure of carbon monoxide, according to the reaction:-

$$SiO_2 + 2C = \underline{Si} + 2CO \qquad \text{.....(1)}$$

The standard free energy change of this reaction may be obtained from the free energy data for silica and carbon monoxide given in Part I, Chapter 3. It is found to be:

$$\Delta G_1^o = 162,600 - 87.7\ T.$$

from which we obtain :-

$$\log_{10} K_1 = 19.17 - \frac{35,540}{T}$$

In the presence of pure silicon and graphite, $K_1 = {}^{a}_{Si} x P_{CO}^{2}$ ($^{a}_{Si}$ being referred to a standard state of pure liquid silicon), so that $^{a}_{Si}$ may be found directly by measuring the equilibrium carbon monoxide pressure of the system at any suitable reaction temperature.

Theexperimental runs were carried out in a molybdenum-wound furnace of the design shown in Fig.26.

Since there is a possibility of some error in the reaction pressure measurements due to silicon monoxide diffusion (due to the effects discussed in Part I, Chapter 3), it would have been preferable to carry out the experiments using a closed graphite crucible. However, the necessity of sampling the metal while molten made this impracticable. The crucible used is shown in Fig.27; this design was found to give the best contact between the liquid metal and both the silica ring and the graphite crucible. The silica ring was formed by baking into position a paste made by mixing a little water glass with crushed quartz. The inside rim of the crucible was curved to facilitate sampling.

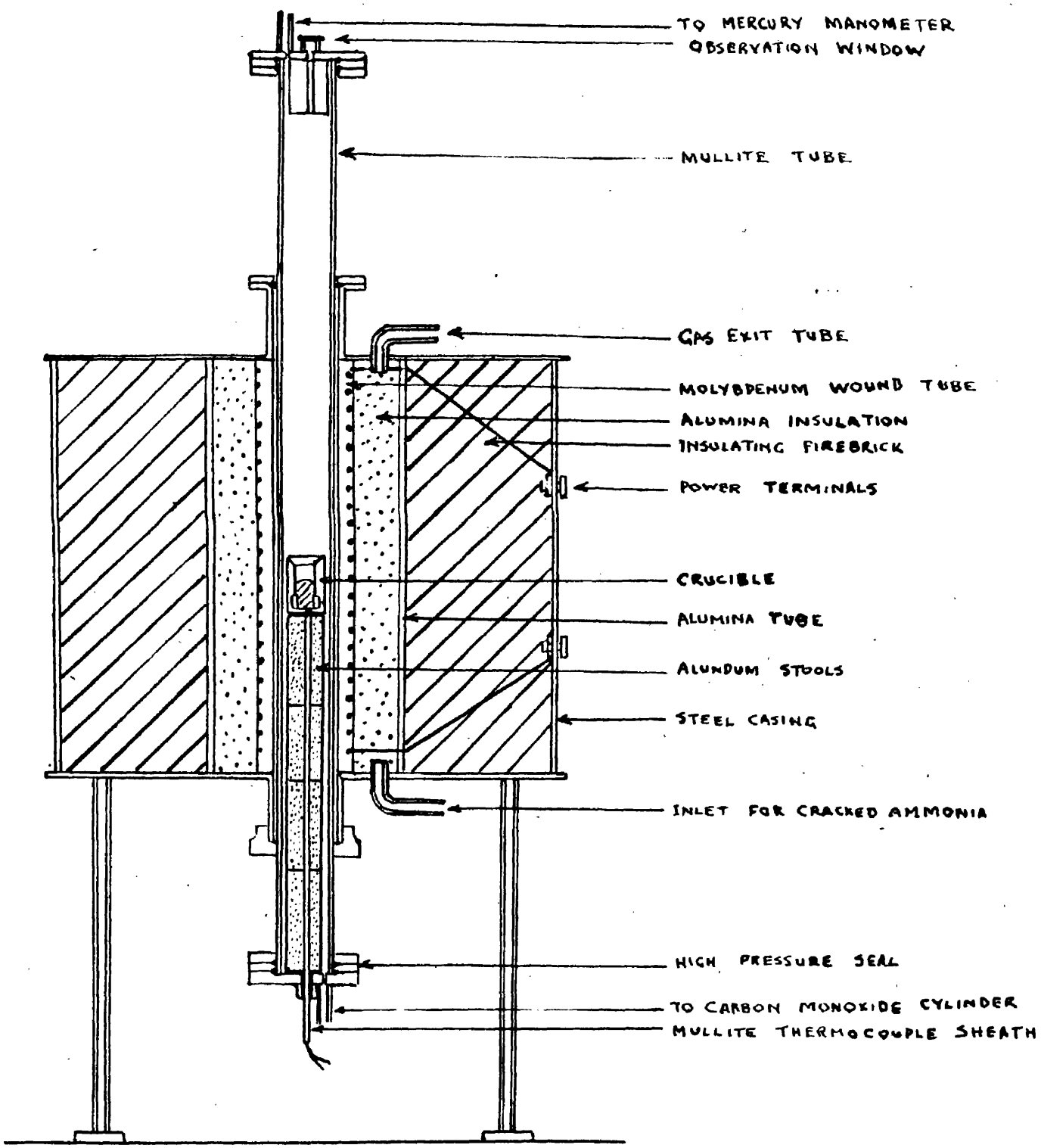


FIG. 26 . MOLYBDENUM WOUND FURNACE

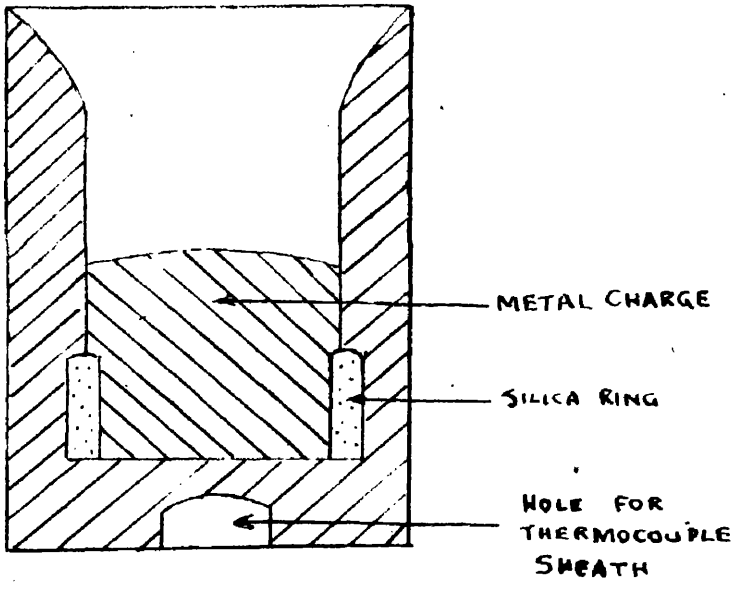


FIG. 27. GRAPHITE CRUCIBLE
(FULL SIZE)

The apparatus was found to operate most successfully at pressures of 1 - 1.75 atmospheres, and the metal compositions and temperatures of the runs were usually adjusted to give pressures in this range. The temperatures used varied from 1375°C to 1500°C.

The metal charges were made up by premelting iron-silicon alloys (made from Armco iron and 98.5 per cent pure silicon), and then saturating these alloys with carbon by heating in a graphite crucible in a high-frequency induction furnace. It was found preferable to use only homogeneous metal samples in the crucible, as mixing of different alloys was found to be very slow.

The equilibrium pressure was measured by observing the pressure changes on a manometer when the furnace temperature was held constant. The furnace atmosphere was purified several times during a run by flushing out with cylinder carbon monoxide. Unless this precaution was taken, nitrogen was found in the furnace gas. This was presumably due to the same causes as were given in Part I, Chapter 4, for the presence of nitrogen during the slag activity measurements.

In earlier runs an attempt was made to establish the equilibrium composition of the metal for a fixed carbon monoxide pressure by observing the changes in silicon content of the metal when the reaction pressure was maintained at the desired value. However, this method was found to be too time-consuming to yield a reasonable number of results, and the quicker procedure of measuring the reaction pressure for a fixed metal composition was therefore adopted. When the equilibrium

had been reached by approach from the high and low pressure directions, the seal on the top of the furnace tube was quickly opened and a metal sample was drawn by suction into a silica tube. This sample was analysed gravimetrically for carbon and silicon. The time required to establish the equilibrium was usually in the range 6-12 hours.

The results obtained are shown in Table XIV.

(3) DISCUSSION OF RESULTS.

As was shown previously, the exact interpretation of silicon activity data in the Fe-Si-C system is impossible without an accurate knowledge of the activity of silicon in the Fe-Si system. However, the experiments of Chipman, Fulton, Gokcen and Caskie(22), and of Ohtani(50) have indicated that carbon and silicon are approximately equivalent on a mole fraction basis. The former work was carried out by the silver distribution experiments already described, and the latter work was done by E.M.F. measurements on a cell of the type Fe-Si-C alloy /silicate slag/ liquid silicon. Although the measurements disagree as to the values of the activity coefficients and their accuracy is difficult to assess, the fact that both sets of data show that carbon and silicon are equivalent in this way, means that this may be taken as a first approximation.

Equivalence of silicon and carbon on a mole fraction basis means that a solution in which $N_{Si} = x$ and $N_C = y$, will have the same silicon activity coefficient as a binary Fe-Si alloy in which $N_{Si} = x + y$.

TABLE XIV.

Results of Silicon Activity Measurements.

No.	T°C	%Si	%C	N_{Si}	N_C	p_{CO}	a_{Si}	γ_{Si}	$-\log\gamma_{Si}$	$N_{Si}+N_C$	$N_{Si}+1.9\ N_C$
1	1375	3.32	3.65	0.057	0.146	1.0	0.0040	0.070	1.155	0.203	0.334
2	1375	2.72	3.97	0.047	0.158	1.41	0.0020	0.0426	1.370	0.205	0.347
3	1425	8.05	2.70	0.136	0.107	1.79	0.0055	0.0405	1.393	0.243	0.339
4	1425	6.8	2.88	0.116	0.114	1.41	0.0089	0.0768	1.114	0.230	0.342
5	1420	8.04	2.5	0.137	0.100	1.41	0.0076	0.0555	1.256	0.237	0.327
6	1420	5.05	3.41	0.086	0.135	1.50	0.0068	0.0791	1.102	0.221	0.342
7	1450	6.29	3.04	0.107	0.121	1.125	0.0274	0.256	0.592	0.228	0.337
8	1450	6.71	2.98	0.114	0.119	1.20	0.0241	0.212	0.674	0.233	0.340
9	1433	8.25	2.48	0.140	0.098	1.07	0.0187	0.134	0.857	0.238	0.326
10	1429	4.35	3.22	0.075	0.130	1.65	0.0071	0.095	1.020	0.205	0.322
11	1466	5.00	3.60	0.084	0.142	1.88	0.0121	0.144	0.842	0.226	0.354
12	1495	15.32	0.88	0.260	0.034	0.947	0.131	0.504	0.298	0.294	0.325
13	1480	13.48	1.27	0.228	0.050	1.30	0.0460	0.202	0.695	0.278	0.323
14	1435	13.54	1.29	0.228	0.051	1.05	0.0208	0.091	1.05	0.279	0.325
15	1420	4.15	3.60	0.071	0.143	2.0	0.0038	0.054	1.252	0.214	0.343

A plot of γ_{Si} against $N_{Si} + N_C$ obtained from ternary alloys should thus coincide with the plot of γ_{Si} against N_{Si} in the binary system.

The composition of the Fe-Si-C alloy in equilibrium with silicon carbide and graphite at 1500°C was measured in the present work by two long runs in which Fe-Si alloys containing initially more than 26 per cent silicon were soaked in a carbon crucible at 1500°C until their composition had become constant. The results obtained are shown in Table XV, in comparison with the results of other workers.

TABLE XV.

Compositions in equilibrium with graphite and SiC.

t°C	%Si	%C	Note
1500°C	23.2	0.25	Present work.
"	24.1	0.34	" "
1540°C	23.6	0.26	Ohtani (50)
"	24.0	0.30	" "
1690	23.7	0.47	Chipman et al(22)
1600	23.1	0.41	"
1490	22.4	0.33	"
1420	21.9	0.28	"

As can be seen from Table XV, agreement is good and the compositions are now considered to be well established. The value of a_{Si} in alloys of these compositions can be calculated from the data on the free energy of silicon carbide obtained in Part I, and the values of $\log \gamma_{Si}$ so obtained at 1420, 1500 and 1600°C have been plotted against $N_{Si} + N_C$ in Fig.25. The value of $\log \gamma_{Si}$ calculated from the free energy data Humphrey et al(25), for 1420°C has also been shown on Fig.25. Since the correction for the carbon content in these alloys is small, the points obtained from the present data are considered to lie very close to the true binary activity coefficient curve for the Fe-Si system.

One point on the binary curve can also be fixed fairly accurately, from data given by Arthur(23) and Taylor(51), who found that a slag of composition 30 per cent lime 28 per cent silica and 42 per cent alumina was in equilibrium at 1500°C with a carbon saturated alloy containing 17.4 per cent silicon and 0.8 per cent carbon. The activity of silica in this slag at 1500°C was measured by the method described in Part I, and a_{SiO_2} was found to be 0.106. From this result a_{Si} in the alloy can be calculated, and the value of $\log \gamma_{Si}$ so obtained has been shown in Fig.25. As with the point fixed by the silicon carbide equilibrium, this point should lie vary close to the activity coefficient curve for the binary system, since the correction for carbon content is small. The approximate silicon activity coefficient curve has been shown on Fig.25, in so far as it can be fixed by these two points, and it can be seen that this new curve is much steeper in the region $N_{Si} = 0.30 - 0.37$ than that obtained by Chipman et al(22).

A possible reason for the error in the latter results, which were obtained by the silver distribution method, is the presence of silver in the iron-silicon phase. It was found that the silver content of this phase rose from 0.2 per cent at low silicon contents to 3.5 per cent in iron containing 38 per cent silicon. From this increase in solubility it follows that the presence of silicon in iron must lower the activity coefficient of silver, and it would therefore be expected that silver would lower the activity coefficient of silicon. The magnitude of this effect is not known, but it could be determined by measuring the composition of the Fe-Si-C-Ag alloy in equilibrium with silicon carbide, graphite and silver. A considerable increase in the silicon content over that found in the absence of silver would indicate that silver does materially decrease the activity coefficient of silicon in iron. If this effect has caused the error in the silver distribution results, the results obtained at low silicon contents should still be fairly accurate.

The values of $\log \gamma_{Si}$ obtained from the present work have also been plotted against $N_C + N_{Si}$ on Fig.25, and it can be seen that they do not fit in well with the tentative new binary curve when plotted in this way. Since the experimental points lie consistently to the left of the binary line, it is clear that carbon has increased the activity coefficient of silicon by a larger amount than would be the case if carbon and silicon were equivalent on a mole fraction basis in their effects on the activity coefficient of silicon. Thus, instead

of the silicon equivalent of carbon, N_{Si}^{C}, being equal to N_C, it must be equal to $x\ N_{Si}^{C}$, where x is greater than 1.

The value of x may be found from the slope of the line obtained when N_{Si}^{C} is plotted against N_C. Before the tentative new activity coefficient curve for the Fe-Si system had been derived, values of N_{Si}^{C} were calculated from the present results using the binary silicon activity coefficients of Chipman et al (22). When plotted against N_C, these values of N_{Si}^{C} showed a very large and unsystematic scatter.

Although exact values of N_{Si}^{C} can only be calculated if the activity coefficient curve for the Fe-Si system is known, an approximate treatment of the present results is possible since they show silicon activities within the almost vertical part of the amended activity coefficient curve, for which $N_{Si} \doteq 0.34$. Approximate values of N_{Si}^{C} can thus be obtained by subtracting the corresponding mole fractions of silicon from 0.34. The values of N_{Si}^{C} obtained from the experimental points in this way have been plotted against N_C in Fig.28. It can be seen that the points can be represented fairly well by a straight line passing through the origin, of slope 1.9. N_{Si}^{C} is thus equal to 1.9 N_C.

From this it is apparent that the activity coefficient of silicon in both binary and ternary alloys should be expressed by a single line when $\log \gamma_{Si}$ is plotted against $N_{Si} + 1.9\ N_C$. All the available data on silicon activities in iron-silicon and iron-carbon-silicon alloys have been plotted in this way, together with the present results, on Fig.29. The sources of the other data used are as follows:-

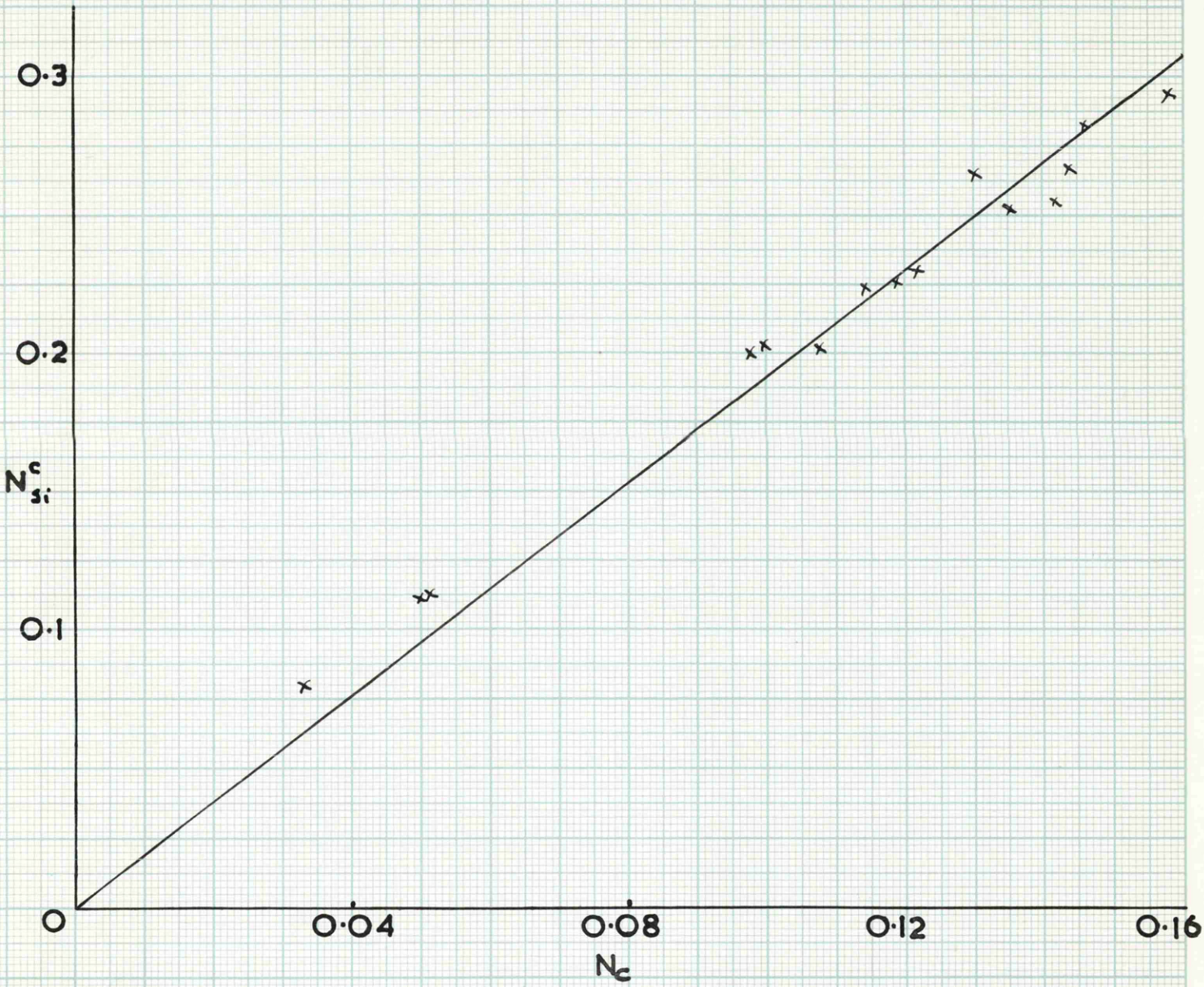


FIG. 28. SILICON EQUIVALENT OF CARBON IN Fe–Si–C ALLOYS

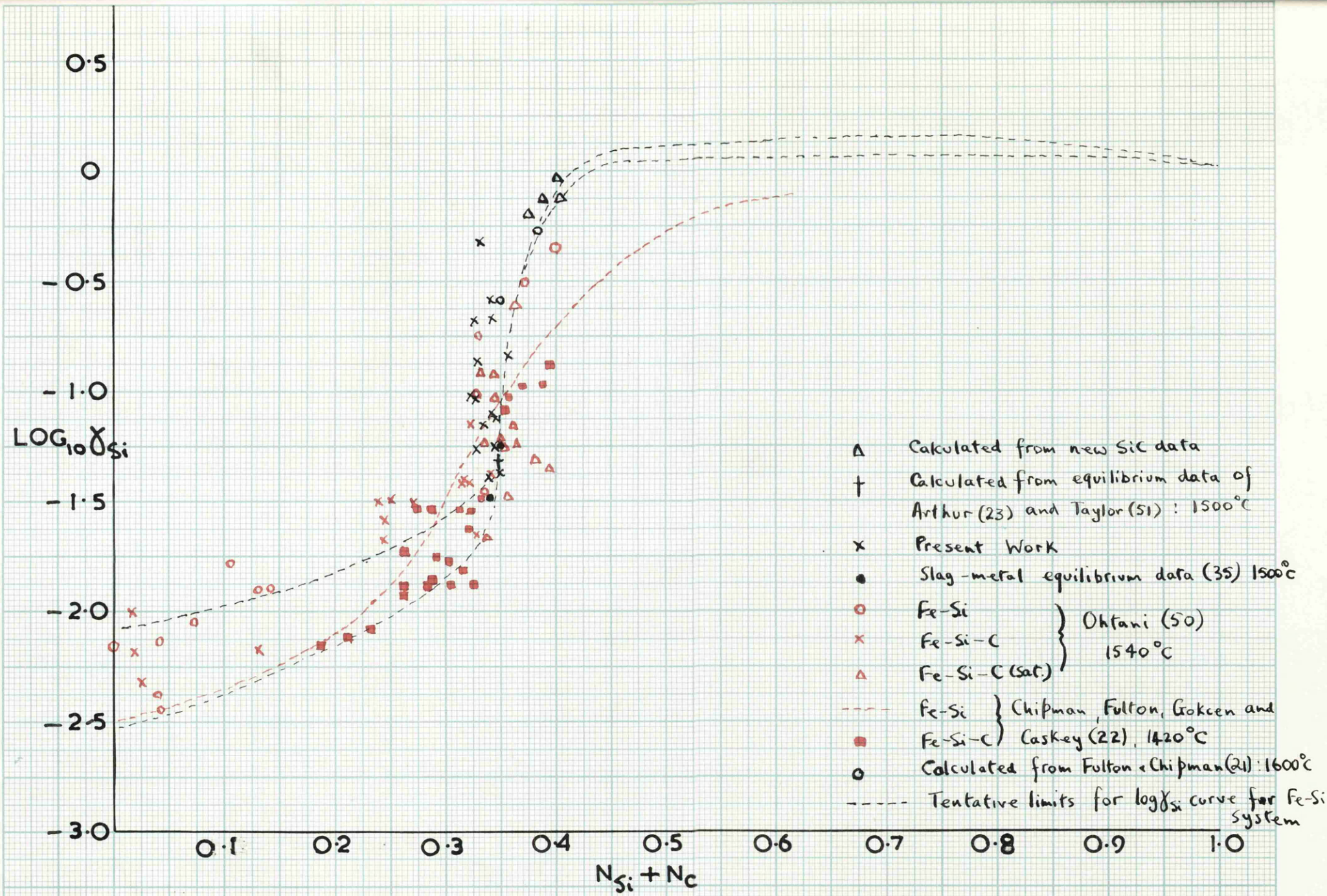


FIG. 29. ACTIVITY COEFFICIENT OF SILICON IN Fe−Si AND Fe−Si−C ALLOYS

(1) Three points were calculated from compositions found by Chipman et al(22) to be in equilibrium with carbon and silicon carbide at 1420, 1500 and 1600°C. The result obtained in the present work at 1500°C has also been plotted, and shows a slightly larger value of $N_{Si} + 1.9\ N_C$ than Chipman's result at the same temperature.

(2) A single point was obtained from the slag-metal data of Arthur(23) and Taylor(51), by the method described previously (page 88). The use of the larger carbon correction has made the proposed silicon activity coefficient curve for the binary system even steeper in this range than was shown in Fig.25.

(3) Activity values over a wide range of compositions were measured by Ohtani(50) at 1540°C, and the results obtained are shown in Fig.29. It can be seen that the results for carbon saturated alloys fall within the steep part of the activity coefficient curve, and are in very good agreement with the present work. The agreement in the case of carbon-free and non carbon saturated Fe-Si-C alloys is not so satisfactory in the region near $\log \gamma_{Si} = -1.5$, but otherwise these results also support the tentative conclusions derived from the present work.

(4) Two results were calculated from slag and metal compositions found to be in equilibrium at 1600°C by Fulton and Chipman(21). The slags were lime-alumina-silica containing 20 per cent alumina, so that the corresponding silica activities could be obtained directly from

the measurements made in Part I. Since the carbon monoxide pressure was 1 atmosphere in Fulton and Chipman's experiments, $K_1 = \frac{a_{Si}}{a_{SiO_2}}$, and from the equation for K_1 given on page 84., the value of K_1 is found to be 1.55 at 1600°C. It is, therefore, possible to calculate the activity of silicon in the metal phase for the two compositions taken. The two points so obtained in the plot of log γ_{Si} against $N_{Si} + 1.9\ N_C$ lie very close to the proposed activity coefficient curve for the binary system.

(5) Two slag-metal equilibrium measurements were carried out at 1500°C in conjunction with the present work(35). As with Fulton and Chipman's experiments, the reaction studied was

$$(SiO_2) + 2C = \underline{Si} + 2CO \quad \text{.....(1)}$$

but in this case the carbon monoxide pressure of the reaction was measured in order to reach equilibrium more quickly than Fulton and Chipman were able to do. The slag compositions were in the range covered by the measurements in Part I, so that the value of a_{Si} in the metal could be calculated directly using the known value of K_1 at 1500°C (0.135). In this case $K_1 = \frac{a_{Si} \times P_{CO}^2}{a_{SiO_2}}$. The two results obtained in this way have been plotted on Fig.29, and can be seen to lie very close to the proposed activity coefficient curve for the binary system at the lower end of the steep portion.

(6) Chipman, Fulton, Gokcen and Caskey's(22) results have also been replotted on Fig.29. The binary silicon activity curve has been represented by a single line, which has a much flatter slope than that

indicated by the new silicon carbide data. Agreement of most of the ternary alloy activities with the present data is quite good, although, as would be expected, the curve tends to slope in accordance with the binary curve obtained by the same method at high silicon activities.

Except for this latter set of data, which were obtained by the silver distribution method, all the above results when plotted a $\log \gamma_{Si}$ against $N_{Si} + 1.9\ N_C$, show a very steep curve in the range $\log \gamma_{Si} = -0.2$ to -1.5. This means that for this wide range in activity coefficients of 0.6 to 0.03, the value of $N_{Si} + 1.9\ N_C$ lies between 0.32 and 0.37. At lower silicon contents the position of the curve is not so well established, Ohtani's(50) E.M.F. measurements indicating higher values of $\log \gamma_{Si}$ than do Chipman's(22) data.

At high silicon contents the possible shape of the curve of $\log \gamma_{Si}$ for Fe-Si alloys is restricted by the fact that a_{Si} must always increase with increasing silicon content but can never become greater than 1. This limits the $\log \gamma_{Si}$ curve as shown in Fig.29 at values of N_{Si} above 0.4.

No temperature effect can be distinguished by examination of the results plotted in the steep part of the activity coefficient curve. Some of the discrepancy which exists between the $\log \gamma_{Si}$ values obtained by Chipman et al.(22) and Ohtani(50) at low silicon contents may, however, be due to the differences in the experimental temperatures used (1420°C and 1540°C respectively). This is the direction of the temperature effect predicted by the calculations of Chipman, Fulton, Gokcen and Caskie(22). A similar increase in activity coefficient

with temperature would be anticipated at high silicon contents and the curves for $\log \gamma_{Si}$ at different temperatures may begin to diverge again in the region of the silicon carbide saturation compositions, where the curves appear to turn sharply.

While more exact treatment of the activity of silicon in Fe-Si-C alloys must await further data on the binary system the treatment given above is considered to be approximately correct. The conclusions obtained differ from previous work in indicating a sharp rise in the value of γ_{Si} in Fe-Si alloys at about $N_{Si} = 0.35$ and a silicon equivalent of carbon of about 1.9 N_C. It is of interest from a practical point of view to consider variations in the silicon and carbon contents of blast furnace iron in the light of these conclusions.

From a consideration of the reaction:-

$$(SiO_2) + 2C = \underline{Si} + 2CO \quad \ldots\ldots\ldots(1)$$

it would be expected that the main factors in determining the silicon content of blast furnace iron would be the silica activity of the slag and the mean temperature of slag and metal, since the value of K_1 for this reaction rises from 0.0178 at 1425°C to 0.135 at 1500°C. However, statistical examination of blast furnace analyses has in several cases failed to establish any significant correlation between silicon content and these two factors(50)(51). Fluctuations in silicon content do take place but no reasons for these fluctuations have as yet been suggested.

The results of the present work suggest that the carbon content of blast furnace iron has a considerable effect on the silicon activity

coefficient in the metal, and may hence have a large effect on the silicon content. The effects of the other constituents on the carbon content of iron at saturation are known, and so the carbon saturation of blast furnace iron may be calculated. It is found that in general the carbon content of blast furnace iron varies from 0.3 to 0.6 per cent below saturation at the prevailing metal temperature. This difference is maintained as the temperature is increased, so that the carbon content of the iron increases with temperature.

The effects of phosphorus, manganese and sulphur on the activity coefficient of silicon are not known, but low-phosphorus pig irons should be approximately comparable with Fe-Si-C alloys of carbon contents about 0.4 per cent below saturation. Using a metal temperature of 1425°C for calculation, the compositions of low and high silicon irons of this type are as follows:-

Low silicon iron	0.4 % Si	4.4 % C.
High silicon iron	1.1 % Si	4.2 % C.

The respective values of $N_{Si} + 1.9\ N_C$ for these two alloys are 0.343 and 0.338, so that both of them lie in the steep part of the activity coefficient curve, and hence are in the range in which large changes in silicon activity are accompanied by quite small changes in $N_{Si} + 1.9\ N_C$.

The variations in the value of a_{Si} at equilibrium which should be produced by the maximum variations in slag composition and temper-

:ature likely to be met with in practice can be estimated. For a slag containing 20 per cent alumina, an increase in lime content from 40 to 48 per cent should be accompanied by a decrease in silica activity from 0.1 to 0.03, and as was noted previously an increase in temperature from 1425 - 1500°C, should produce a sevenfold increase in a_{Si} in the metal if the slag composition remains unchanged. These variations are, of course, much larger than would be expected in any single furnace, where a variation in a_{Si} ofthe order of three to four times might be expected. If the shape of the tentative silicon activity curve derived in this work is correct, a change in a_{Si} of this order would be expected to result in only a small change in $N_{Si} + 1.9\ N_C$, and since the carbon content of the iron is found in practice to increase with temperature, a decrease of silicon content with increasing temperature is not necessarily impossible. A poor correlation of silicon content with slag composition and furnace temperature is therefore to be expected, especially if fluctuations in the carbon content of the iron take place which are unconnected with these factors.

Control of the silicon content of blast furnace iron would thus be expected to depend mainly on the inter-relationship between silicon and carbon in the iron. However, since the mechanism of carbon and silicon pick-up in the blast furnace is not known, no method is at present apparent by which these two variables could be altered to obtain the required silicon control in the blast furnace.

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